STUDIES ON METAL CHELATES

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SAURASHTRA UNIVERSITY
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IN
THE FACULTY OF SCIENCE (CHEMISTRY)

BY

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(M.Sc.)

UNDER THE GUIDANCE
OF

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RAJKOT - 360 005.
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Ph. D.
Thesis

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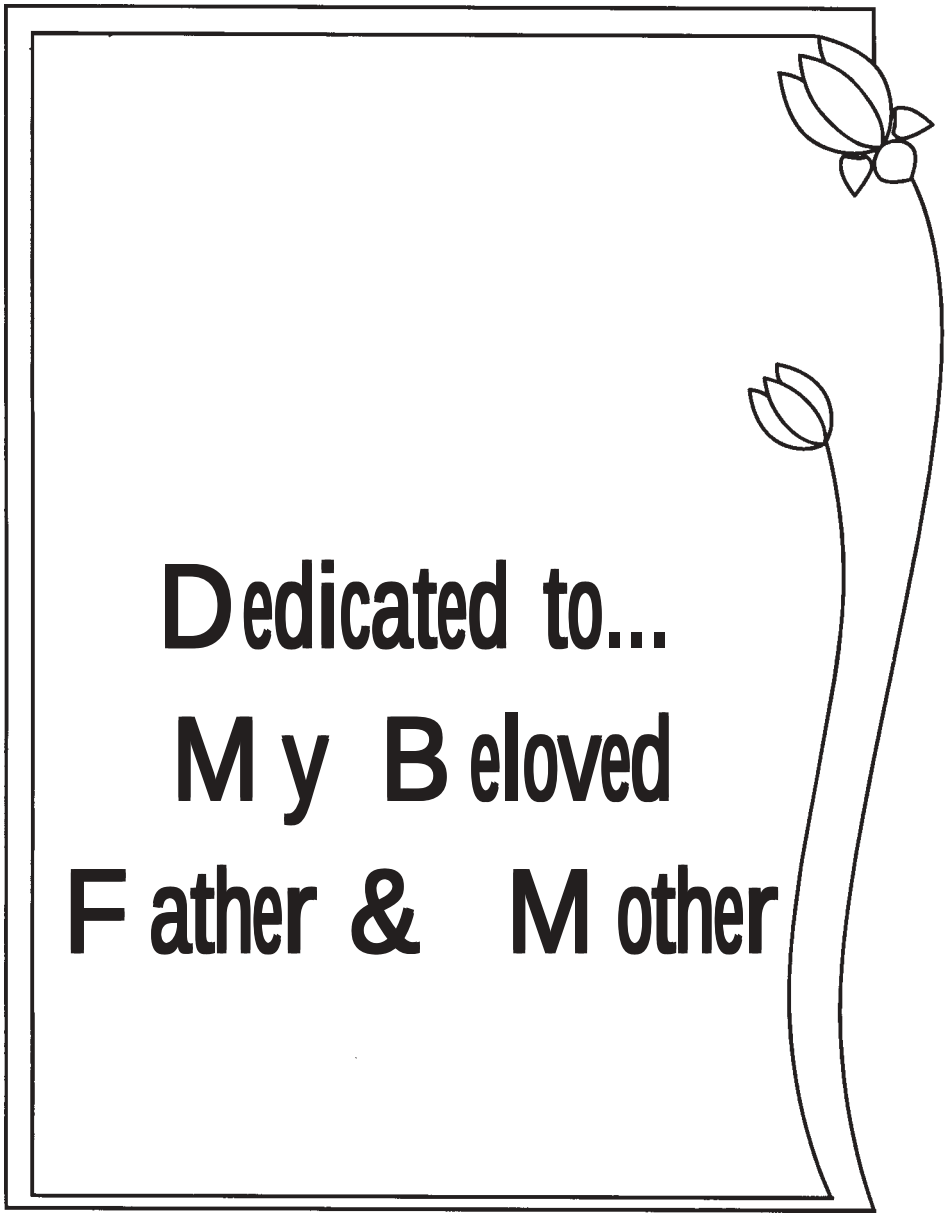
Dedicated to...
My Beloved
Father & Mother

ACKNOWLEDGEMENT

I wish to make devote supplication to THE ALMIGHTY for hisbenediction, but for HIS inspiration this task would not have been accomplished.

I express my deep sense of gratitude to my eminent guide **Rtd. Prof. U. V. Manvar**, M. Sc., Ph. D., Ex. Dean of Science Faculty, Department of Chemistry, Saurashtra University - Rajkot for his propaedeutical teaching, sagacious guidance, creative criticism, perpetual encouragement and painstaking expert supervision throughout the research work which brought my efforts to fruition.

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I wish to express my sincere gratitude to Late Dr. G. K. Joshi for helping me whenever I was confronted with problems; he was always with me to overcoming them.

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- I. I. T. - Chennai (ESR)
- Forensic Science Laboratory - Junagadh (UV)

for providing necessary instrumental facilities.

I am at a loss to find words to express my feelings in acknowledging the tremendous debt that I owe to my father **Late Mr. M. K. Mayatra** and mother **Somiben**. It is only because of their blessing, continuous encouragement and inspiration that I have been able to steer through the stresses and strains of this study. My thank are also due to kind and affectionate inspiration and amiability from my brothers **Ramnikbhai, Jayantibhai, Vinodbhai, Dhirajbhai** and **Kishor** & Bhabhi, Jyotsnabhabhi, Ranjubhabhi, Bharti & Nilam.

I specially mention thanks to my wife **Saraswati** & My Baby **Mahek** for cooperating during my work, .

I gratefully appreciate the affection and co-operation extended to me by my senior and lovable colleagues Dr. M. D. Vaghela, Dr. R. C. Khunt, Dr. C. R. Kanzariya, Dr. B. M. Vadher, Dr. Yogesh Naliapara, Dr. Mausam Chavda.

I am heartly thankful to Pravin, Manvar, Bhavesh, Rathodbhai, Ketan, Ankur, Sagar and my all other colleagues who have helped me directly or indirectly for the completion of my research work.

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Finally, I am thankful to Saurashtra University - Rajkot for providing research work.

(Manish M. Mayatra)

CANDIDATE'S STATEMENT

I hereby declare that the work incorporated in the present thesis entitled "STUDIES ON METAL CHELATES" is an original and has not been submitted to any other University / Institution for the award of any degree or diploma. I further declare that the results presented in the thesis, consideration made therein, contribute in general to the advancement of knowledge in chemistry.

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Gujarat - INDIA

CERTIFICATE

This is to certify that MR. MANISH M. MAYATRA (Regd. No. 2371 Date : 25-9-1999) has carried out the work presented in the thesis entitled 'STUDIES ON METAL CHELATES" is an original piece of work under my supervision. It has not been submitted to any other University / Institution for any degree or diploma. I recommend this thesis for submission for the award of Doctor of Philosophy in Chemistry.

Place : Rajkot

Date :

Rtd. PROF. U. V. MANVAR

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INTRODUCTION

INTRODUCTION

Chetation and Biological systems

The term chelale is applied to those compounds that result from a combination of an electron donor with a metal ion to form a ring structure. The compounds capable of forming a ring structure with a metal are designated as ligands. If the metal is bonded to carbon, the ring structure is not a chelate but an organometallic compound which has different properties. If the metal is not in a ring, the compound is called simply a metal complex. Nearly all the metals can form chelates and complexes. However, the electron donor atoms in the chelating agent are limited entirely to N, 0 and S. If the complex forming ligand supplies both electrons for chelation, then the bond is classified as a co-ordinate covalent bond and by convention is represented as M←X, where M is the metal and X is ligand. If one electron is supplied by the metal and one by the ligand (normal covalent bond), the bond is shown as M–X.

The size of the rings in chelate compounds is of interest with respect both to stability and occurance. Three-membered rings have not been identified, but 4-membered rings are known, and 4- membered rings containing sulfur may be quite stable. The 5- and the 6-membered chelate rings are most common and usually show the greatest stability. The chelates are identified by a number of properties, no one of which constitutes positive identification. so evidence from as many different sources as possible is desirable.

The "normal" chemical reactions of a metal ion in solution disappear if a chelate is formed.The chelate may serve to prevent precipitation of an ion which normally would precipitate. For example, the cupric ion in basic Fehling's solution normally would be precipitates as cupric hydroxide but is prevented from doing so by the formation of the copper tartrate chelate. In this case, the formation of the chelate results in an increased water - solubility. In other cases, the chelate

may be insoluble in water and soluble in organic solvents. Water - soluble chelating agents, called sequestering agents, often used to remove objectionable metal ions by combining with them to form stable water soluble chelates.

Deferoxarniiie mesylate (Desferal), a trihydroxamic acid compound made up of the elements of 3 moles of a 1,5 -pentamethylene diamine, 2 moles of succinic acid and one of acetic acid is isolated from streptomyces pilosus[1]. The compound combines with Fe^{+++} to form a water-soluble chelate which is excreted by the kidneys. The agent removes excess iron from the tissues but does not displace it from essential proteins (e.g. transferrin) involved in the iron transport mechanism. The compound is reported to be selective for iron with little or no affinity for calcium, copper and other metals[2,3]. It is nontoxic and has been used successfully in the treatment of primary (hereditary) and secondary hemochromatosis and as effective antidote for the treatment of acute iron poisoning in children.

The reddish-colored iron chelate of deferoxamine has a high stability constant ($\log K_S = 30.7$) which may be attributed to its unique chemical structure in which the iron is octahedrally bound by the hydroxamic acid oxygen atoms and carbonyl oxygens of the ligand.

Like penicillamine, EDTA is able to form water-soluble metal chelates in the body which may be excreted readily. The free acid and sodium salts of EDTA, when administered to mammals, produce an excessive loss of essential body calcium and are quite toxic. The calcium-disodium salt (edathamil) is comparatively nontoxic and serves as an effective antidote for the treatment of lead poisoning. It is also reported to be effective as an antidote for other heavy metals, including copper, chromium, iron and nickel.

Numerous drugs unrelated to form chelate complexes with metals; and although the complex formation may have no direct relation with the major action of the drug, it may be responsible for significant side-effects. Thus, the antitubercular agent, thiacetazone, may produce an onset of diabetes mellitus, and it has been suggested that this may be due to its ability to chelate with zinc in the beta cells of the pancreas, thereby inhibiting the production of insulin. Diphenyldithiocarbazone, oxine and alloxan are believed to react in the same manner to produce a diabetogenic effect. The anemia produced by administration of the hypotensive agent hydralazine (Apresoline) has been attributed to its ability to complex with iron[5]. Dimercaprol and the antitubercular drug isonicotinic acid hydrazide (INH) tend to induce histaminer like actions and it has been suggested that this may be due to complexing with a copper-catalyzed enzyme responsible for the destruction of histamine[6]. INH may function as a chelating agent inhibiting the growth of Mycobacterium tuberculosis, but the evidence for this mode of action not conclusive. The drug is an active chelating agent and derivatives, such as 1-methyl-isonicotinoyl hydrazine, which are unable to chelate are inactive[7]. The salicylates, catechol amines, biguainides, tetracyclines and many other commonly used drugs form metal chelates. Boric acid chelates with the 3,4-hydroxy groups of epinephrine and related catechol amines without altering the pharmacologic properties[8].

Oxidation - Reduction Potentials and Biological Action

The orientation of surface active molecules at the surface of water or at the interface of polar and nonpolar liquids takes place with the monopolar (e.g. hydrocarbon) portion of the molecule oriented toward the vapour phase or nonpolar liquid and the polar groups (e.g. -COOH, -OH, $-NH_2$, $-NO_2$, etc.) towards the polar liquid. Three forces are involved in orientations of this type : namely van der Waals' forces, hydrogen bonds and ion dipoles. Vander attraction between the nonpolar groups tending to hold the hydrocarbon groups together.

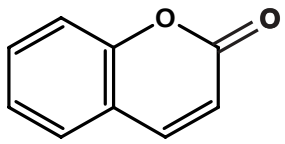
The antibacterial activity of high molecular weight quaternary ammonium compounds (cationic soaps) appear to be dependent on two or more factors such as (1) the charge density on the nitrogen atom (2) the size and the length of the nonpolar groups attached to the nitrogen and (3) the lipophilic hydrophilic balance. The fact that the lower and excessively high molecular weight compounds are inactive indicates that more than a charged nitrogen in necessary for aniibacterial activity. The active compounds are those in which the charged nitrogen in unsymmetrically positioned in the molecule, therefore long nonpolar chains appear to be a necessary structural feature. This suggests that the most active compounds will be those having a maximum charge on an unsymmetrically positioned nitrogen and lipophilic hydrophilic balance to impart optimum surface activity. Molecules of this type will be attracted and held comparatively firmly to the bacterial cell wall by the cation reacting with anionic cellular groups to form reinforced ionic bonds and the nonpolar portion of the molecule associating through vander Waals bonds. This action occurs below the CMC.

Like the soaps the quaternary ammonium compounds can form mixed micelles. Thus the bactericidal concentration of dedecyl (C_{12}) dimethyl benzyl ammonium must be doubled in the precence of 25 percent of hexadecyl (C_{16}) dimethyl benzyl ammonium chloride[9]. Albert[10] interpreted this findings in terms of mixed micelle formation. His reasoning may be stated briefly as follow : Drugs act in their monomolecular form, but at the CMC and above the micelle compites with the microorganism for the monomers, thereby reducing the effective antibacterial concentration.

Surface-active agents can be expected to have a pronounced effect on the permeability of die cell. Mildly surface-active agents may be adsorbed as a monolayer on the cell membrane and thereby interfere with the absorption of other compounds though this membrane or may alter membrane structure and functions. Many central nervous system depressant drugs, such as the hypnotic sedative, anticonvulsant and central relaxant agents possesess the general structure of nonionic surface-active compounds.

An Overview of Coumarins

The coumarins are large group of naturally occuring oxygen heterocycles. In 1820, Vogel[11] reported the isolation of coumarin from tonka beans, bearing the characteristic aroma of cattled grass. Later on an identical compound coumarin (I) was synthesized in 1868 on treatment of sodium salt of o-hydroxy benzaldehyde with acetic anhydried by W. H. Perkin Sr.[12-14]



(I)

Extensive studies were carried out on isolation and structure elucidation of naturally occurring coumarins and it was reviewed by many researchers[15-18] including spath[19]. Reppel[20], Karrer[21], Dean[22] Sheshadri and Vishwapoul[23] and Murray[24].

Further coumarin and its annelated derivatives are reported to possess significant antibacterial[25], coronary dilatory[26] and hypothermia activities[27]. Therefore, it became of interest to synthesize new derivatives of these system of expected biological activities. The use of the readily obtainable 3-acetyl coumarin, seemed to be a logical and easy route for the synthesis. The relations of 3-acetyl coumarin with different reagents resulted in the synthesis of several annelated coumarin derivatives which are needed for a biological activity programme.

Coumarin contains the parent nucleus of benzo α-pyrane. They occur in plants of the families like Orchidaceae, Leguminaceau, Rutaceae, Umbelliferae and Libaiac[28]. Some of the coumarins show distinct physiological, photodynamic and bacteriostatic activity[29-31]. They have been put to many diverse used[32]. Their chelating characteristics have long been observed and the bacteriostatic activity seems to be due to chelations. 4-hydroxy coumarin, known as benzotetronic acid because of its striking similarity with 5-membered tetronic acid[33] acts as anti-coagulant agent.

The physicochemical studies[34-38] of the coumarins with chelating groups at appropriate position and their metal complexes reveal that the ligands of coumarin are used as potential analytical reagents. Magnetic and spectral studies have been also carried out[38-39]. The scope of the present review is to briefly describe the preparation and applications of the analytical useful coumarins.

Various 3-substituted 4-hydroxy coumarin derivatives are studied for its pharmacological properties. However the physiological active compounds have various other substituents.

4-hydroxy coumarin residues substituted at 3-position proved essential for biological activity in 1948 after synthesizing over 150 compounds were studies. Later, 4-hydroxy coumarin are found not only as an anticoagulant but also as rodenticide by Wisconsion, Alumni Research Foundation.

Acetyl derivatives are prepared[40-47] by acetylation of different derivatives of 4-hydroxycoumarin in presence of acetic acid and $POCl_3$ to give 3-acetyl-4-hydroxycoumarin derivatives, on its further reaction with ethyl acetate in presence of sodium to give 3- acetoaceyl-4-hydroxy coumarin derivatives[40,46-50] were obtained.

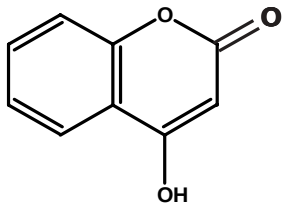
The utilization of 3-acetoacetyl 4- hydroxycoumarin as a fascile system was first reported by Klosa[51] & co-workers.

Anschutz[52] reported the first synthesis of 4-hydroxycoumarin in 1903. Though a few natural 4-hydroxy coumarins have been reported two antibiotics, such as novobiocin[53] and coumermycin[54] with a 4-hydroxycoumarin structure have been isolated. As a result, several methods for its synthesis have been developed and also anticoagulants like tromexan[55], Warfarin[56], Cyclimarol[57], mercoumar[58] came into market.

Various methods have been developed for the synthesis of 4-hydroxycoumarins and their substituted derivatives are summarized as below:

(1) Anschutz method[59]
(2) Kaneyuki method[60]
(3) Pauly-Lockmann synthesis[61]
(4) Robertson synthesis[62]
(5) Sonn's synthesis[63]
(6) Mentzer Synthesis[64]
(7) Garden's method[65]
(8) Ziegler and Junek method[66]
(9) Resplandy's method[67]
(10) Jain Rohatagi and Sheshadri's method[68]
(11) Shah, Bose and Shah's method[69]
(12) Thakar & Shah[70]

Some 4-hydroxy coumarins(II) have been prepared by the method of Shah and co-workers[70] in good yield by condensation of different phenol with malonic acid in the presence of freshly fused zinc chloride and phosphorous oxychloride. The method is useful as a single preparation of 4-hydroxy coumarin derivatives substitution at benzenoid part.



(II)

Their synthesis is considered to be of two main types. In one case phenol with an orthocarbonyl group of its derivatives are utilized and 2 or 3 carbon atoms of the α-pyran system is from another moiety. In the other case, a phenol is used and 2,3,4 carbon atoms of the hetero ring comes from malonic acid or its derivatives.

Literature survey reveals that 4-hydroxycoumarin and its derivatives are most widely used as drugs. Many people synthesized hydroxy coumarin derivatives like 3-acetyl-4-hydroxycoumarin[40],3-acetoacetyl-4-hydroxy coumarin[40], Esculetin (5,7 dihydroxycoumarin)[71] 4-methylesculetin (4- methyl-6,7-dihydroxycoumarin)[71], 4-phenylesculetin(4-phenyl-6,7dihydroxy coumarin)[72], Daphnetin (7,8-dihydroxycoumarin)[73], 4-methyl-daphnetin (4-methyl-7,8-dihydroxycoumarin)[74], 3-phenyldaphnetin (3-phenyl-7,8-dihydroxy coumarin)[73-75], 4-phenydaphnetin(4-phenyl-7,8-dihydroxy coumarin)[76], 3-benzyl-4,5-dihydroxycoumarin[77], OBTA (oximidobenzotetronic acid)[78]. NHBC (3-nitroso-4-hydroxyl-5,6 benzocoumarin)[78-80] and AHMC (3-amino-7-hydroxy-4-methylcoumarin)[81-82].

The chalcones are natural biocides[83] and are well known intermediates in the synthesis of heterocyclic compounds exhibiting various biological activities on the other hand coumarins also show activity such as antifungal[85], anticoagulant[86], antibacterial[87] and insecticidal[88]. Chalcones are coloured compounds because of the presence of the chromophore auxochrome. The term "Chalcones" was first coined by Kostanecki[89] who did pioneering work in the synthesis of natural colour compounds.

In view of the above observations, we thought of preparing some new chalcones of 4-hydroxy coumarins which also may have any of the above activity. Since chalcones are the precursor of flavone and possess antiinvasive activity[90-93] Corresponding to flavones and flavanones, chalcones of 4-hydroxy coumarin were prepared by different methods.

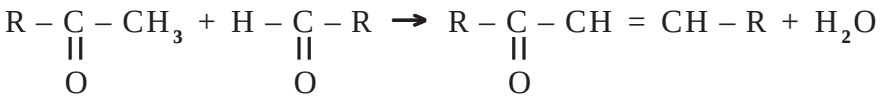
The chalcones of 4-hydroxycoumarin are prepared from 3-acetyl-4-hydroxycoumarin[94,95] via Claisen condensation with different aromatic aldehydes such as benzaldehyde and anisaldehyde. The above compounds give colouration of $FeCl_3$.

Chalcones react with a number of metal ions and are reported to be more reactive than the aldehyde or ketone from which they have been prepared[95]. This reaction has been exhibited for the detection of Fe(II) by 2',4'-dihydroxy chalcone provided the concentration of interesting ions kept at a minimum 2',3',4' trihydroxy chalcone was used as an analytical reagent.

For amperometric estimation of copper[97] and for spectrophotometric study of the germanium[98], Bhardwaj and Singh[99] introduced 2'-hydroxyl-2',5'-dichloro-4'-methyl benzal acetophenone oxime as an analytical reagent for Cu (II), Ni (II) and Pd (II).

Various methods of synthesis have been used for synthesis of chalcones. A general method for synthesis of chalcone consist in condensing an appropriate aldehydes. The most convenient method is the one that involves the Claisen-Schmidt condensation of equimolar quantities of a aryl methyl Ketone with aryl aldehyde in presence of alcoholic alkali[100].

Several condensing agents used are alkali of different strength[101-102], hydrogen chloride[103-104], phosphorous oxychloride[105], piperidine[106], anhydrous acid[110], aluminium chloride[107], boron triflouride[108], aqueous solution of borax[109] and perchloric acid[111], During course of this reaction, a water molecule is eliminated



The chalcones can be prepared by

(i) Friedel crafts cinnamoylation

(ii) Nencki reaction with an aromatic compound

(iii) Fried rearrangement of aryl cinnamates

(iv) Diazo coupling of phenyl diazonium chloride with benzoylacrylic acid.

The chalcone have been found to be useful providing the structures of natural products like homolock, tennin[112], cyanomaclurin[113], ploretin[114], eriodictoryl[115] and homoeriodictoryl naringenin[116], etc.

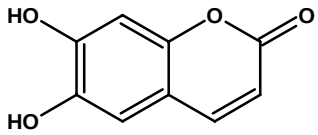
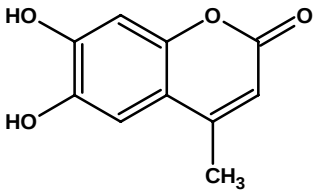
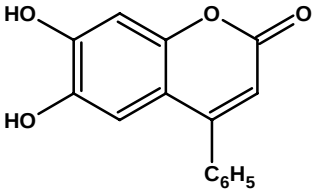
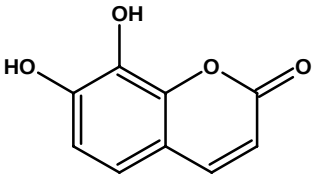
The chalcones are intermediate compounds useful for the synthesis of various heterocyclic compounds like flavanone, flavones, benzal coumarinones, anthrocyanins as well as certain compounds like deoxybenzoin and hydantoins which are found to have some therapeutic importance as antispasmodic and mydriactices.

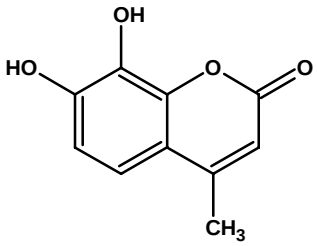
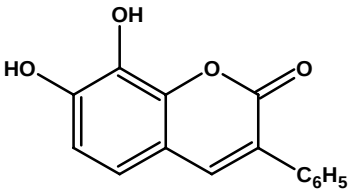
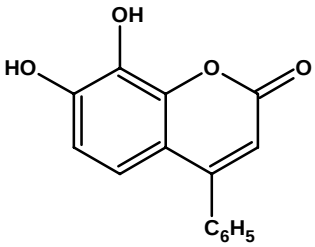
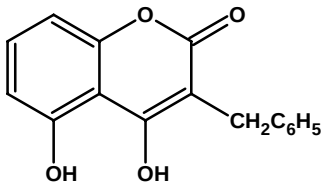
Schraufstatter and Deutsen[117] and Calcuieri[118] observed antibacterial properties of some chalcones. Vibhute[119] have reported antimicrobial activity of some halochalcones and flavones. Brodsher Brown and Blue[120] prepared chalcones have been suggested as remedy for cancer[121-122].

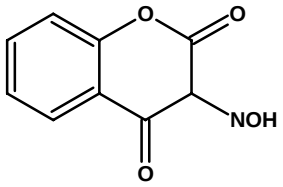
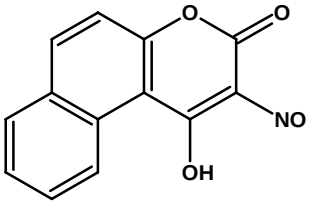
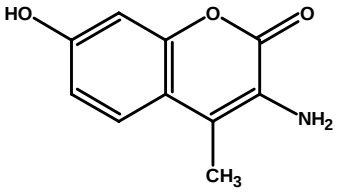
ANALYTICAL APPLICATIONS :

Analytical applications of Hydroxycoumarins

Here (d) detection (s) spectrophotometric determination (g) gravimetric determination

Sr. No.	Hydroxycoumarins	Metal detected determined	Reference
1	 Esculetin (6,7-Dihydroxycoumarin)	Fe(III) (d) Fe(III) (s) Mo(VI) (s) Nb(V) (s) Ti(IV) (s)	123 124 125 126 127
2	 4-Methylesculetin (4-Methyl-6,7-dihydroxycoumarin)	Mo(VI) (s) Pb(V) (s) Ti(IV) (s)	125 126 127
3	 4-Phenylesculetin (4-Phenyl-6,7-dihydroxycoumarin)	Mo(VI) (s) Zr(IV) (s) Ti(IV) (g)	125 128 128
4	 Daphnetin (7,8-Dihydroxycoumarin)	Mo(VI) (s) Ti(IV) (s)	34 128

Sr. No.	Hydroxycoumarins	Metal detected determined	Reference
5	 4-Methyldaphnetin (4-Methyl-7,8-dihydroxycoumarin)	Mo(VI) (s) Nb(V) (g) Th(IV) (g) Ta(V) (g) Ti(IV) (g)	34 130 131 130 130
6	 3-Phenyldaphnetin (3-Phenyl-7,8-dihydroxycoumarin)	Mo(VI) (s) UO_2(II) (s)	132 133
7	 4-Phenyldaphnetin (4-Phenyl-7,8-dihydroxycoumarin)	Mo(VI) (s) Nb(V) (g) V(IV) (s) Ta(V) (g) Ti(IV) (g) Zr(IV) (g)	34 134 136 134 135 137
8	 (3-Benzal-4,5-dihydroxycoumarin)	Ti(IV) (s) UO_2(II) (s)	132 133

Sr. No.	Hydroxycoumarins	Metal detected determined	Reference
9	 OBTA (Oximidobenzotetronic acid)	Co(II) (s) Co(III) (g) Cu(II) (s) Fe(II) (s) Fe(II) (g) Ru(III) (s) Rh(III) (s) Pd(II) (g) Os(IV) (s) Ir(IV) (s) Pt(IV) (s)	140-141 142-143 145 145-146 147 148 148 149 36 36 36
10	 NHBC (3-Nitroso-4-hydroxy-5,6-benzocoumarin)	Co(II) (s) Co(II) (d) Cu(II) (s) Fe(II) (d) Fe(II) (s) Ir(IV) (s) Ni(II) (s) Ru(III) (s) Rh(III) (s)	150 151 152 153 38 38 154 155 156
11	 AHMC (3-Amino-7-hydroxy-4-methylcoumarin)	Cu(II) (g)	157

From the survey, it is conclude that 4-hydroxycoumarins are useful as analytical reagents. They give sensitive color reactions and can be made selective by appropriate variation in pH or alcohol concentration and the use of suitable masking agents. Coumarin can be also used as flourescent probes in the study of membrance and of protein preparations[158]. They have been employed with advantages in detection and determination of many metals by spectrophotometric and gravimetric techniques. Several analytically significant separations and subsequent estimations have been made with their aid. Recently some of the hydroxycoumarins have been used as chromagenic sparying reagents in inorganic chemicals analysis[159-160].

Literature survey shows that many type of activities have been done on 3-acetyl-4-hydroxycoumarin and 3-acetoacetyl-4-hydroxycoumarin derivatives, but no more work has been done as a chelating agents for metal ions. There is no information available regarding the characteristic properties and activity of metal complexes of 3-acetyl-4hydroxycoumarin and 3-acetoacetyl-4-hydroxycoumarin derivatives.

PRESENT WORK

Keeping on view of fact that 3-acetyl-4-hydroxycoumarin its chalcone derivatives are also good chelating agents as well as there is a large scope open yet to disclose about the characteristics properties and activity of their metal complexes. We have proposed to synthesize some new 3-acetyl-4-hydroxycoumarin, its chalcone derivatives acting as ligands and further synthesizing their metal complexes.

In present study we have synthesized some new 3-acetyl-4-hydroxycoumarin derivatives its chalcone derivatives capable of forming metal complexes as mentioned in chapter-I and also synthesized their metal complexes. The characteristic properties of metal complex have been studied as mentioned in chapter - II to V of Part - I.

The metal ions selected are Cu(II), Ni(II), Co(II) and Fe(II).

The entire work is presented in two parts. Part - I comprises of five chapters. Chapter-I includes the synthesis of ligands and their characterization by elemental analysis and spectral studies. Chapter II to V include the synthesis and analytical studies of Cu(II), Ni(II), Co(II) and Fe(II) complexes. Part-II includes the potentiometric deterimination of stepwise stability constants of metal complexes. Lastly the general discussion is presented.

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PART - I

SYNTHESIS AND ANALYTICAL STUDY OF 4-HYDROXY COUMARIN DERIVATIVES AS LIGANDS AND THEIR METAL COMPLEXES

It is presented in five chapters.

CHAPTER - 1 : It deals with synthesis of 4-hydroxy coumarin derivatives and their characterization by elemental analysis and spectral studies.

CHAPTER - 2 to 5 : It deals with synthesis and analytical studies of Cu(II), Ni(II), Co(II) and Fe(II) complexes.

PART - I
SYNTHESIS AND ANALYTICAL STUDY OF 4-HYDROXY COUMARIN DERIVATIVES AS LIGANDS AND THEIR METAL COMPLEXES

CHAPTER - 1
SYNTHESIS AND ANALYTICAL STUDY OF 4-HYDROXY COUMARIN DERIVATIVES AS LIGANDS

CHAPTER -1

The following ligands have been synthesized.

(1) 3-[{3-(2'-chloro) phenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-AX)

(2) 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-BX)

(3) 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-DY)

(4) 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-EY)

They have been charaterized by the following techniques :

(I) Elemental analysis.

(II) Absorption spectra in UV and Visible region.

(III) IR spectral studies.

(IV) NMR spectral studies.

(V) MASS spectral studies.

Experimental

SYNTHESIS OF LIGANDS

It involves the following steps.

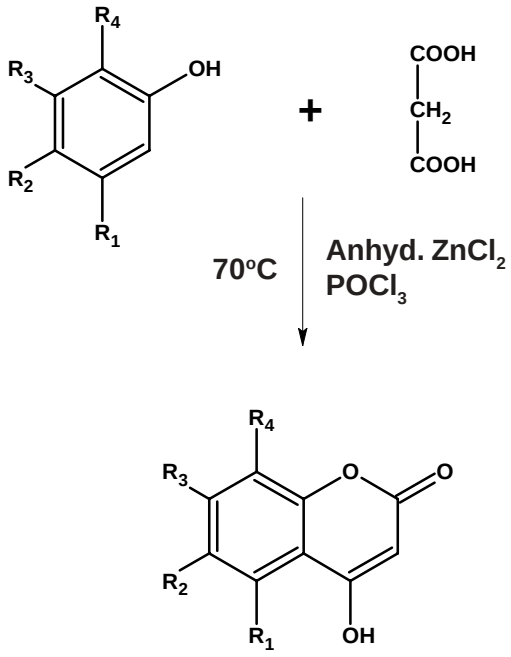
[A] Synthesis of 4-hydroxy-6-chloro-7-methylcoumarin :[69,80]

p-Chloro m-cresol (14.2g., 0.1 Mole) and malonic acid (10.4 g., 0.1 Mole) were added to a mixture of phosphorous oxychloride (40ml.) and anhydrous zinc chloride (30g.) which was pre heated to 60-70^{o}C and the reaction mixture was heated on a water bath at 70^{o}C for 12 hrs. It was cooled and decomposed with ice and water to afford solid, which was filtered and washed with water. It was then treated with 10% sodium carbonate and filtered. The filterate was slowly acidified with diluted hydrochloric acid. At the neutral point, the precipitates obtained are filtered and product was washed with water and further dried and recrystallized with methanol as light cream colour compound. Yield 85%, M.P. 236-37^{o}C

[B] Synthesis of 4-hydroxy-6-methylcoumarin :[69,80]

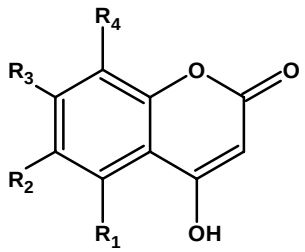
p-Cresol (15.0g., 0.1 Mole) and malonic acid (10.4 g., 0.1 Mole) were added to a mixture of phosphorous oxychloride (40ml.) and anhydrous zinc chloride (30g.) which was pre heated to 60-70^{o}C and the reaction mixture was heated on a water bath at 70^{o}C for 16 hrs. It was cooled and decomposed with ice and water to afford solid, which was filtered and washed with water. It was then treated with 10% sodium carbonate and filtered. The filterate was slowly acidified with diluted hydrochloric acid. At the neutral point, the precipitates obtained are filtered and product was washed with water and further dried and recrystallized with methanol as light cream colour compound. Yield 72%, M.P. 253^{o}C.

Reaction Scheme



Sr. No.	R_1	R_2	R_3	R_4
1.	H	Cl	CH_3	H
2.	H	CH_3	H	H

Physical constants of substiuted 4-hydroxycoumarins



Sr. No.	Substitution				Molecular Formula	Reaction Time (hrs.)	Molecular Weight (g./mol)	Melting Point ^{0}C	Rf Value	Solubility
	R_1	R_2	R_3	R_4						
1.	H	Cl	CH_3	H	$C_{10}H_7O_3Cl$	12	210	236-37	0.56	Methanol
2.	H	CH_3	H	H	$C_{10}H_8O_3$	16	176	253	0.52	Methanol

The compound is soluble in hot DMSO

TLC solvent system : Ethyl acetate : Hexane (5 : 5)

SYNTHESIS OF LIGANDS

[B] Synthesis of 3-acetyl-4-hydroxycoumarin derivatives[50,55]

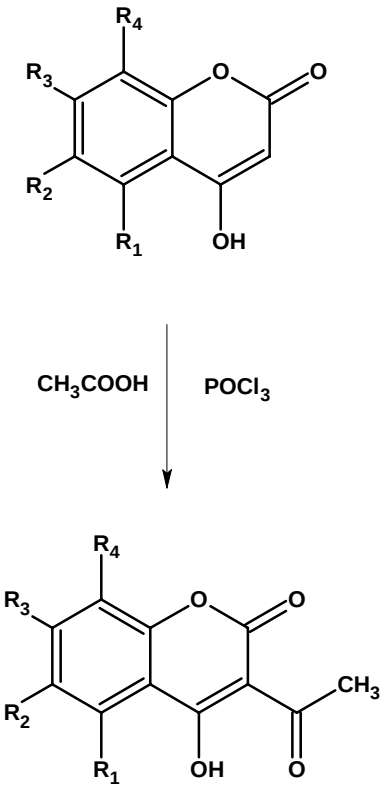
(1) 3-Acetyl-4-hydroxy-6-chloro-7-methylcoumarin

4-Hydroxy-6-chloro-7-methylcoumarin (1g.) was dissolved in acetic acid (5ml.), phosphorus oxychloride (4ml.) and the reaction mixture was refluxed gently for 60-70 min. and then added to ice water. The product was filtered, washed with water and crystallized with alcohol as yellow (slight) colour compound. M.P. 210^{o}C, Yield 88%.

(2) 3-Acetyl-4-hydroxy-6-methylcoumarin

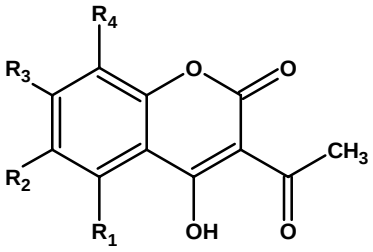
4-Hydroxy-6-methylcoumarin (1g.) was dissolved in acetic acid (5ml.), phosphorus oxychloride (4ml.) and the reaction mixture was refluxed gently for 60-70 min. and then added to ice water. The product was filtered, washed with water and crystallized with alcohol as yellow (slight) colour compound. M.P. 145^{o}C, Yield 76%.

Reaction Scheme



Sr. No.	R_1	R_2	R_3	R_4
1.	H	Cl	CH_3	H
2.	H	CH_3	H	H

Physical constants of substiuted 3-acetyl-4-hydroxycoumarins



Sr. No.	Substitution				Molecular Formula	Molecular Weight (g./mol)	Melting Point ^{0}C	Rf Value	Solubility
	R_1	R_2	R_3	R_4					
1.	H	Cl	CH_3	H	$C_{12}H_9O_4Cl$	252	210	0.49	Methanol
2.	H	CH_3	H	H	$C_{12}H_{10}O_4$	218	145	0.56	Methanol

The compound is soluble in hot DMSO

TLC solvent system : Ethyl acetate : Hexane (5 : 5)

SYNTHESIS OF LIGANDS

[C] Synthesis of 3-Acetyl-4-hydroxy-6-chloro-7-methyl coumarin derivatives[104]

(1) 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one

A mixture of 3-acetyl-4-hydroxy-6-chloro-7-methyl coumarin (2.52 gm, 0.01M); o-chloro-benzaldehyde (0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was reflux on water bath for 4 hrs., cooled and solid was separated. Them it was crystallised from suitable solvent, as redish yellow colour compound M.P. 220^{o}C, yield 69%.

(2) 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one

A mixture of 3-acetyl-4-hydroxy-6-chloro-7-methyl coumarin (2.52 gm, 0.01M); p-chloro-benzaldehyde (0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was reflux on water bath for 4 hrs., cooled and solid was separated. Them it was crystallised from suitable solvent, as redish yellow colour compound M.P. 210^{o}C, yield 75%.

SYNTHESIS OF LIGANDS

[D] Synthesis of 3-Acetyl-4-hydroxy-6-methyl coumarin derivatives[104]

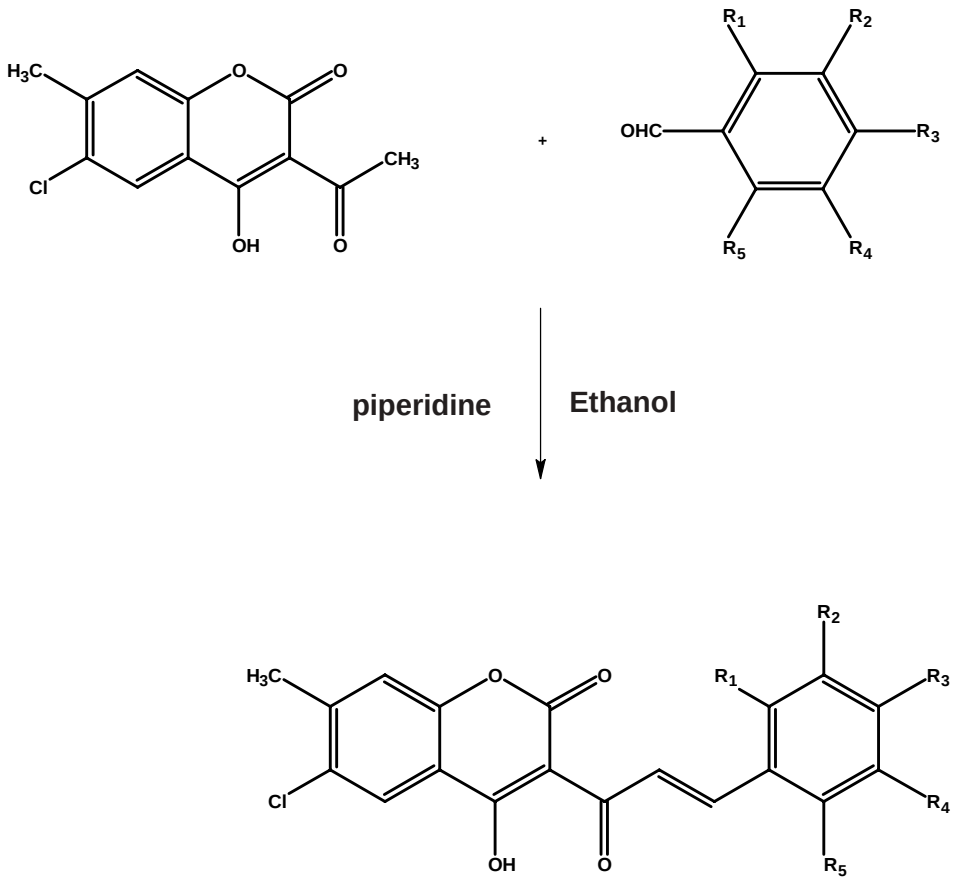
(1) 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl coumarin

A mixture of 3-acetyl-4-hydroxy-6-methyl coumarin (2.52 gm, 0.01M); o-chloro-benzaldehyde (0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was reflux on water bath for 4 hrs., cooled and solid was separated. Them it was crystallised from suitable solvent, as redish yellow colour compound M.P. 153^{o}C, yield 78%.

(2) 3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-methyl coumarin

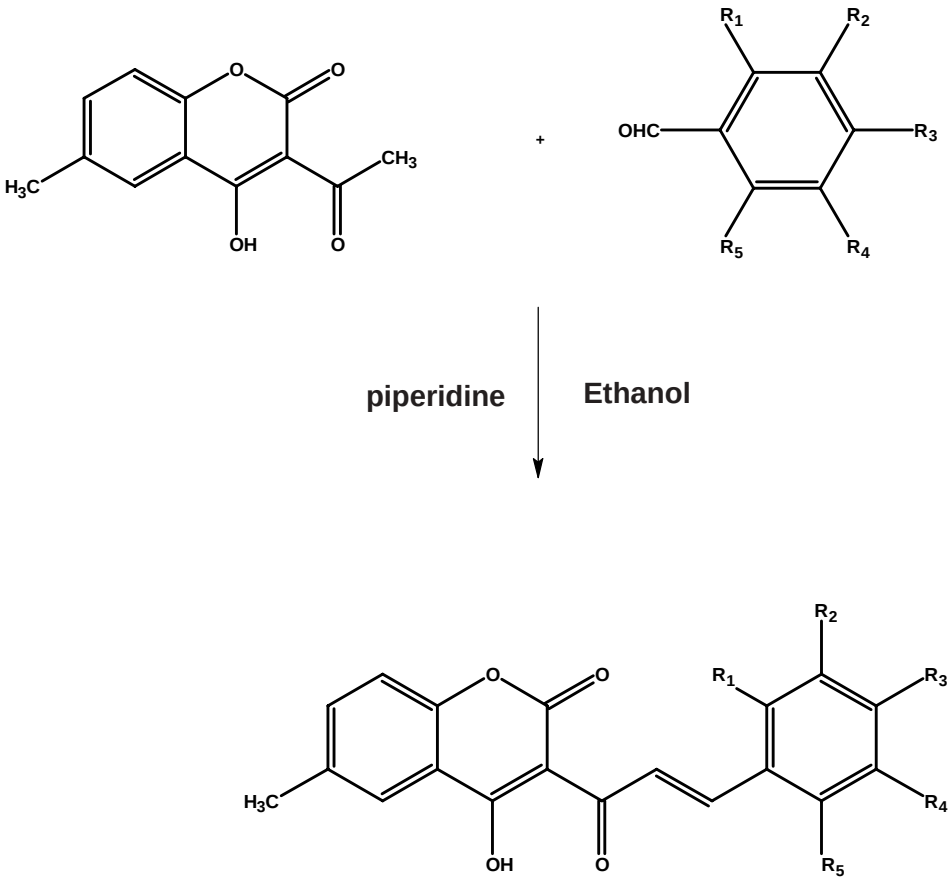
A mixture of 3-acetyl-4-hydroxy-6-methyl coumarin (0.4 gm, 0.01M); p-chloro-benzaldehyde (0.025 M) and piperidine (1 ml) were added into ethanol (50 ml). The reaction mixture was reflux on water bath for 4 hrs., cooled and solid was separated. Them it was crystallised from suitable solvent, as redish yellow colour compound M.P. 220^{o}C, yield 80%.

Reaction Scheme



Sr. No.	R_1	R_2	R_3	R_4	R_5
1.	Cl	H	H	H	H
2.	H	H	Cl	H	H

Reaction Scheme



Sr. No.	R_1	R_2	R_3	R_4	R_5
1.	Cl	H	H	H	H
2.	H	H	Cl	H	H

Characterisation of the ligands

(I) Elemental analysis:

Carbon and hydrogen were estimated on a Coleman C-H Analyzer. The results are summarized in Table-I on page 36.

(II) Absorption spectral study :

Absorprtion spectra of the ligands solution in DMF (known concentration) were recorded on a Backmann Spectrophotometer. They are presented in Table-II on page 37. The nature of absorption curves are show in Fig. 1A & 1B on page 50,51.

(III) NMR spectral study:

The Nuclear Magnetic Resonance Spectrum of the ligands were recorded in TFA solution on BRUKER (300 MHz) Spectrometer. The results obtained are presented on Table - IIIA to IIIE on page 38 to 41. The nature of NMR spectra are shown in Fig. 2A to 2E on page 52 to 55.

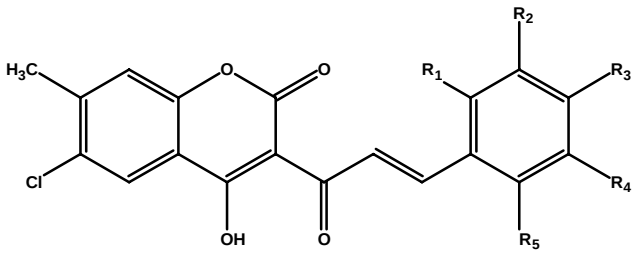
(IV) IR Spectral study :

The Infrared spectra of the ligands were recorded on Shimadzu 435-IR Spectrophotometer between 4000-400 cm^{-1}. The results are presented in Table - IV A to IVE on page 42 to 45. The IR spectras are show in Fig. 3A to 3E on page 56 to 59.

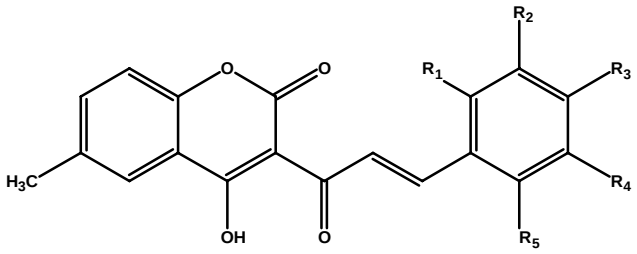
(V) MASS spectral study:

The Mass Spectrum of the ligands were on VG 70-S, LRMS-1000 R.P. Spectrometer. The fragmentation pathways are presented on page 46 to 49 and corresponding Mass spectra are show in Fig. 4A to 4E on page 60 to 63.

TABLE - I : Physical constants and analytical data of ligands



(X)



(Y)

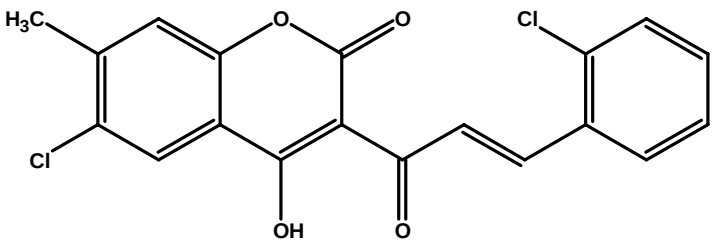
SR. NO.	NAME OF LIGAND	MOLECULAR FORMULA	MOLECULAR WEIGHT	% OF CARBON		% OF HYDROGEN	
				FOUND	CAL	FOUND	CAL
1.	Chal-AX	$C_{19}H_{12}O_4Cl_2$	375	60.92	60.96	3.15	3.20
2.	Chal-BX	$C_{19}H_{12}O_4Cl_2$	375	60.92	60.96	3.15	3.20
3.	Chal-DY	$C_{19}H_{13}O_4Cl$	341	65.65	65.69	5.08	5.11
3.	Chal-EY	$C_{19}H_{13}O_4Cl$	341	71.40	71.43	4.73	4.76

TABLE - II

Absorption maximum (λ max) and log ε of ligands

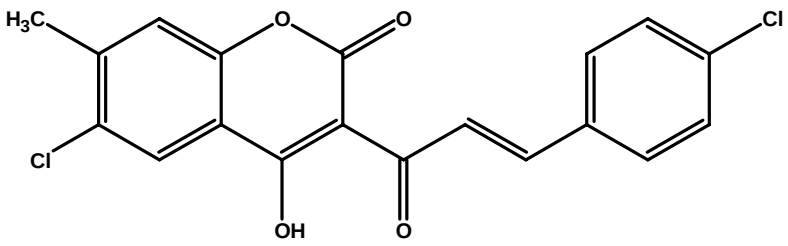
Sr. No.	LIGAND	λ max nm	log ε
1.	Chal-AX	339.2	3.198
		314.0	3.748
		293.6	3.788
		279.2	3.749
2.	Chal-BX	350.0	2.807
		308.0	3.469
		293.6	3.538
		280.4	3.505
3.	Chal-DY	324.8	1.616
		287.6	1.650
		268.4	1.606
4.	Chal-EY	348.8	2.753
		328.4	2.499
		290.0	2.395

TABLE - III A : Chalcone - AX



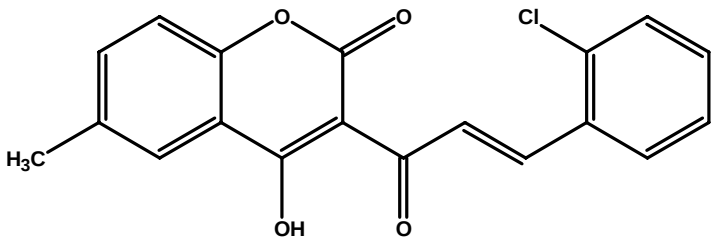
SIGNAL NO.	SIGNAL POSITION VALUE	RELATIVE NO. OF PROTON	MULTIPLICITY	INFERENCE
1.	2.49	3H	Singlet	$-CH_3$
2.	6.12 to 8.46	6H	Multiplet	Ar-H
3.	8.06	1H	Doublet	Ar-CH=
4.	8.08	1H	Doublet	=CH-Ar

TABLE - III B : Chalcone - BX



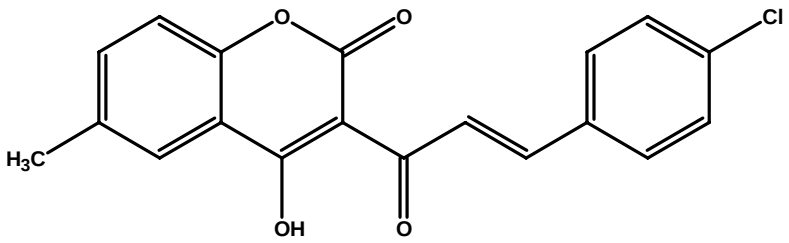
SIGNAL NO.	SIGNAL POSITION VALUE	RELATIVE NO. OF PROTON	MULTIPLICITY	INFERENCE
1.	2.53	3H	Singlet	$-CH_3$
2.	7.43	2H	Doublet	Ar-2H
3.	7.64	2H	Doublet	Ar-2H
4.	8.04	1H	Doublet	Ar-HC=
5.	8.09	1H	Doublet	=HC-Ar
6.	8.29-8.36	2H	Multiplet	Ar-H & Ar-H

TABLE - III D : Chalcone - DY



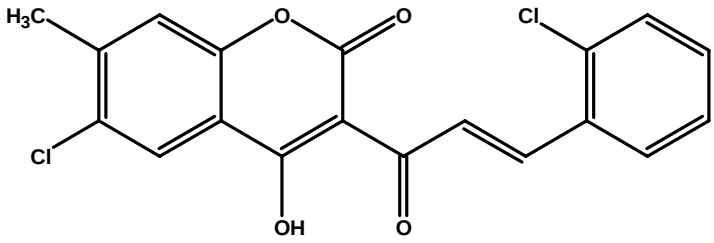
SIGNAL NO.	SIGNAL POSITION VALUE	RELATIVE NO. OF PROTON	MULTIPLICITY	INFERENCE
1.	2.45	3H	Singlet	$-CH_3$
2.	7.19 to 8.51	7H	Multiplet	Ar-H
3.	8.07	1H	Doublet	Ar-CH =
4.	8.09	1H	Doublet	= CH-Ar

TABLE - III E : Chalcone - EY



SIGNAL NO.	SIGNAL POSITION VALUE	RELATIVE NO. OF PROTON	MULTIPLICITY	INFERENCE
1.	2.42	3H	Singlet	$-CH_3$
2.	6.67	2H	Doublet	Ar-2H
3.	7.27	2H	Doublet	Ar-2H
4.	7.09	1H	Doublet	CH=CH
5.	7.17	1H	Doublet	CH=CH
6.	7.40-7.48	2H	Multiplet	2H-Ar
7.	7.69	1H	Doublet	1H-Ar

TABLE - IV A : Chalcone - AX



(1) Frequency Range : 4000-400 cm^{-1}

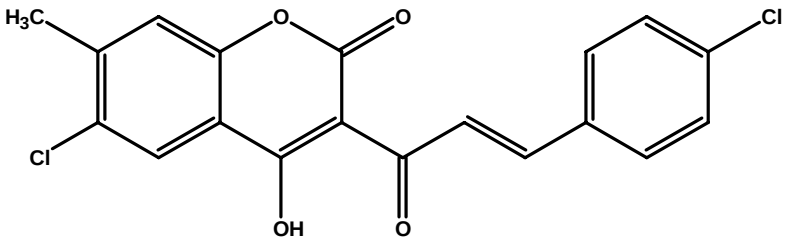
(2) Instrument : Shimadzu 435 IR

(3) Sample Technique : KBr Pallet

(4) Spectrum on Page : 56

Type	Vibration mode	Frequency in cm^{-1} (observed)
Hydroxy -OH	O-H str.	3398
	-OH band.	1319
Alkane-CH_3	C - H str. (asym.)	2923
	C - H str. (sym.)	2854
	C - H def. (asym.)	1438
	C - H def. (sym.)	1382
-CH	C - H str.	3066
	C - H band.	1292
Aromatic	C = C str.	1577
	C - H i.p. def.	1213
	C - H.O.O.P. def.	860
Ketone	C = O str.	1710, 1670
Halogen	C- Cl str.	729

TABLE - IV B : Chalcone - BX



(1) Frequency Range : 4000-400 cm^{-1}

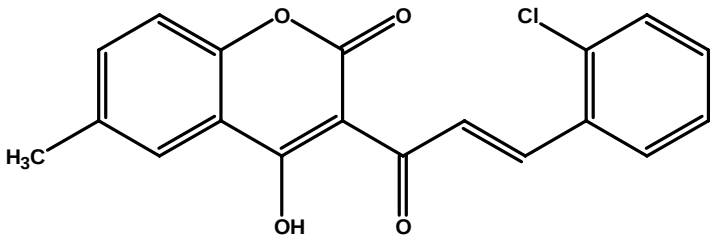
(2) Instrument : Shimadzu 435 IR

(3) Sample Technique : KBr Pallet

(4) Spectrum on Page : 57

Type	Vibration mode	Frequency in cm^{-1} (observed)
Hydroxy -OH	O-H str.	3425
	-OH band.	1382
Alkane-CH_3	C - H str. (asym.)	2925
	C - H str. (sym.)	2854
	C - H def. (asym.)	1434
	C - H def. (sym.)	1382
-CH	C - H str.	3055
	C - H band.	1203
Aromatic	C = C str.	1529
	C - H i.p. def.	1290
	C - H.O.O.P. def.	866
Ketone	C = O str.	1726,1682
Halogen	C- Cl str.	756

TABLE - IV D : Chalcone - DY



(1) Frequency Range : 4000-400 cm^{-1}

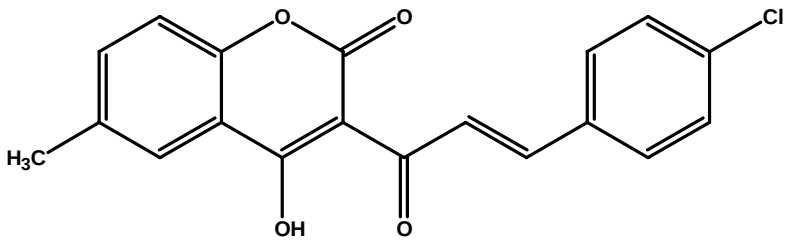
(2) Instrument : Shimadzu 435 IR

(3) Sample Technique : KBr Pallet

(4) Spectrum on Page : 58

Type	Vibration mode	Frequency in cm^{-1} (observed)
Hydroxy -OH	O-H str.	3406
	-OH band.	1242
Alkane-CH_3	C - H str. (asym.)	3081
	C - H str. (sym.)	2923
	C - H def. (asym.)	1438
	C - H def. (sym.)	1385
-CH	C - H str.	3083
	C - H band.	1242
Aromatic	C = C str.	1575
	C - H i.p. def.	1099
	C - H.O.O.P. def.	832
Ketone	C = O str.	1703, 1687
Halogen	C- Cl str.	725

TABLE - IV E : Chalcone - EY



(1) Frequency Range : 4000-400 cm^{-1}

(2) Instrument : Shimadzu 435 IR

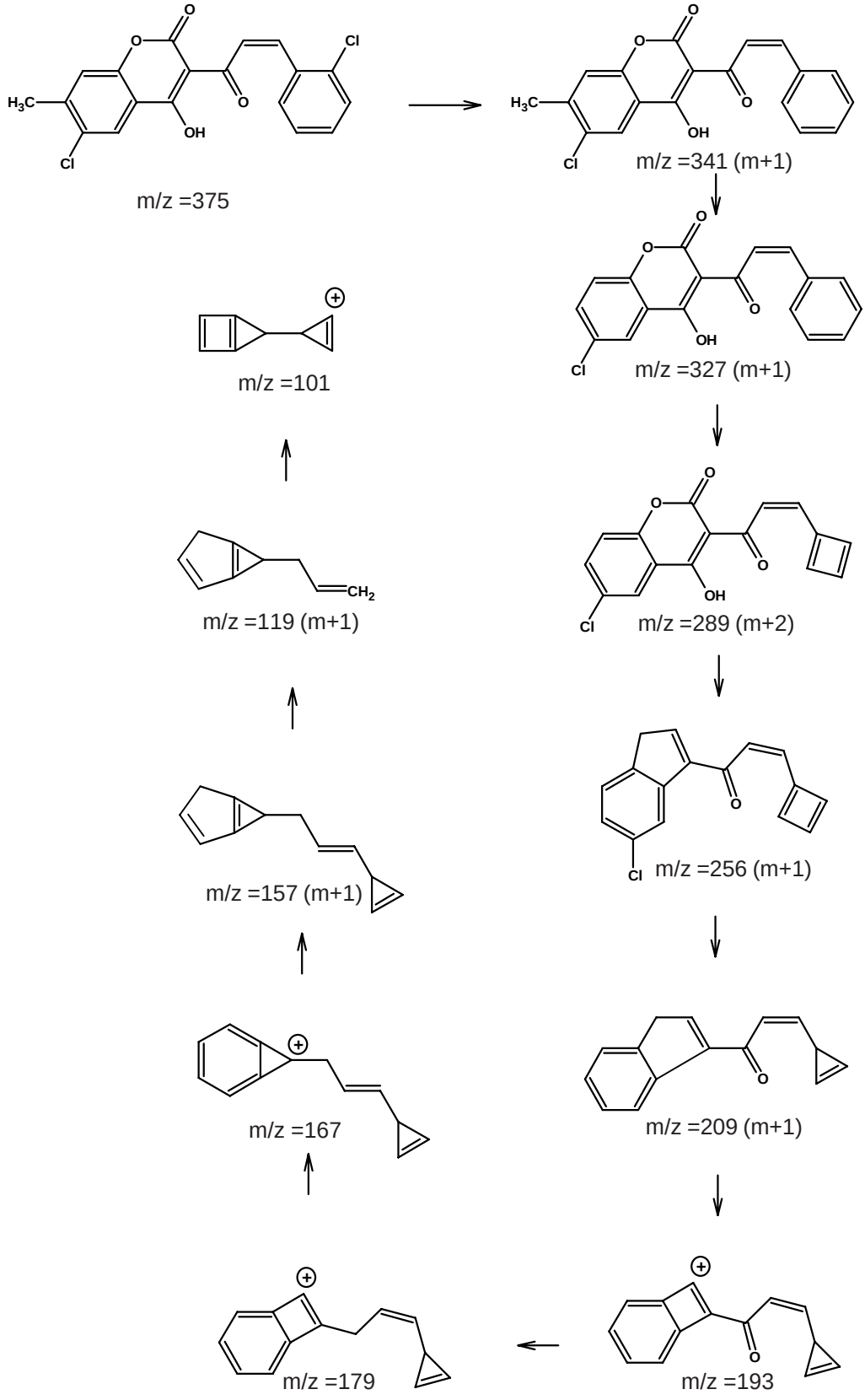
(3) Sample Technique : KBr Pallet

(4) Spectrum on Page : 59

Type	Vibration mode	Frequency in cm^{-1} (observed)
Hydroxy -OH	O-H str.	3375
	-OH band.	1310
Alkane-CH_3	C - H str. (asym.)	2923
	C - H str. (sym.)	2852
	C - H def. (asym.)	1423
	C - H def. (sym.)	1385
-CH	C - H str.	3026
	C - H band.	1261
Aromatic	C = C str.	1525
	C - H i.p. def.	1234
	C - H.O.O.P. def.	827
Ketone	C = O str.	1701, 1681
Halogen	C- Cl str.	725

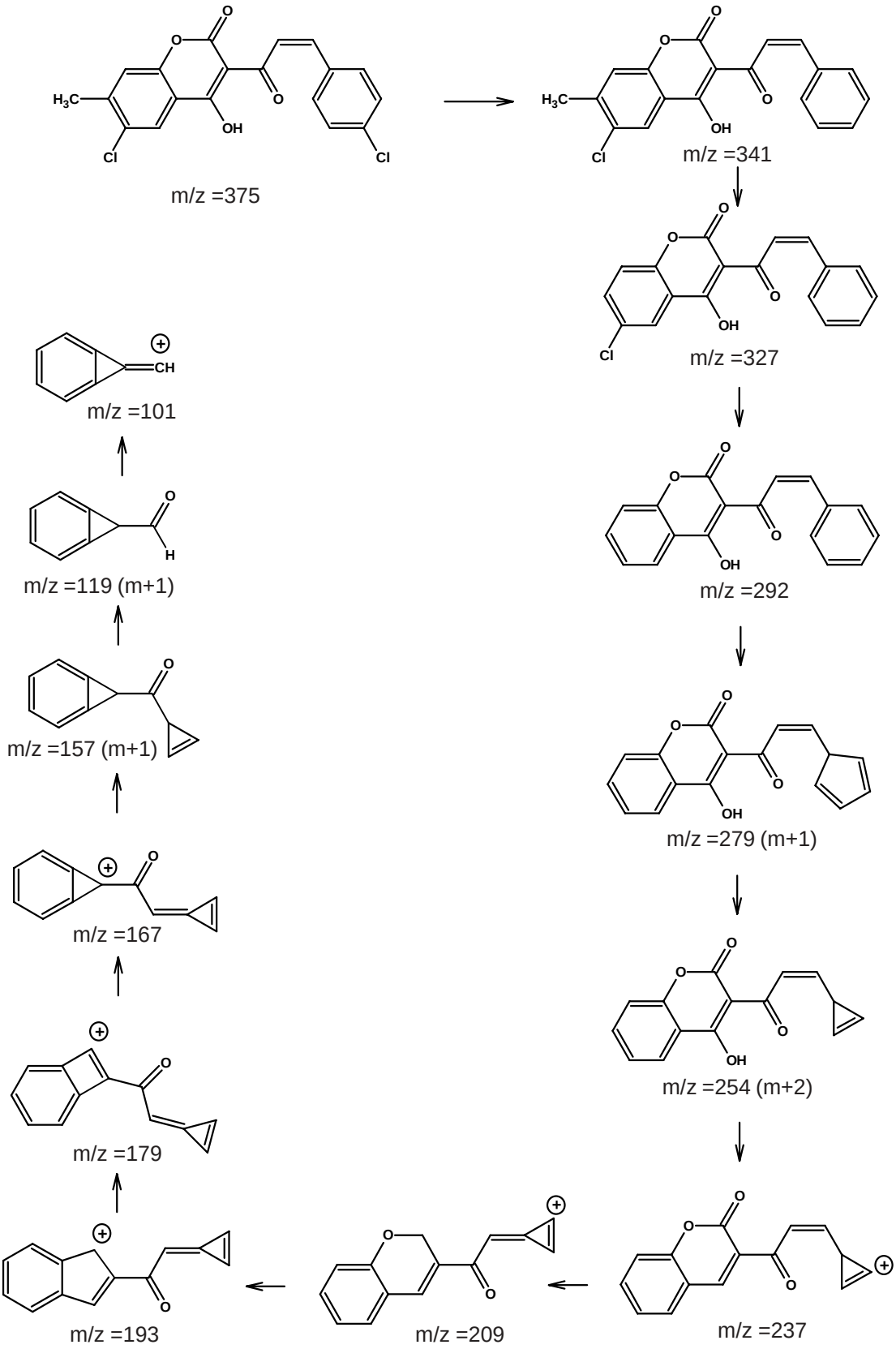
Mass spectral analysis of 3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-AX)

Possible fregmentation pathways is shown below.



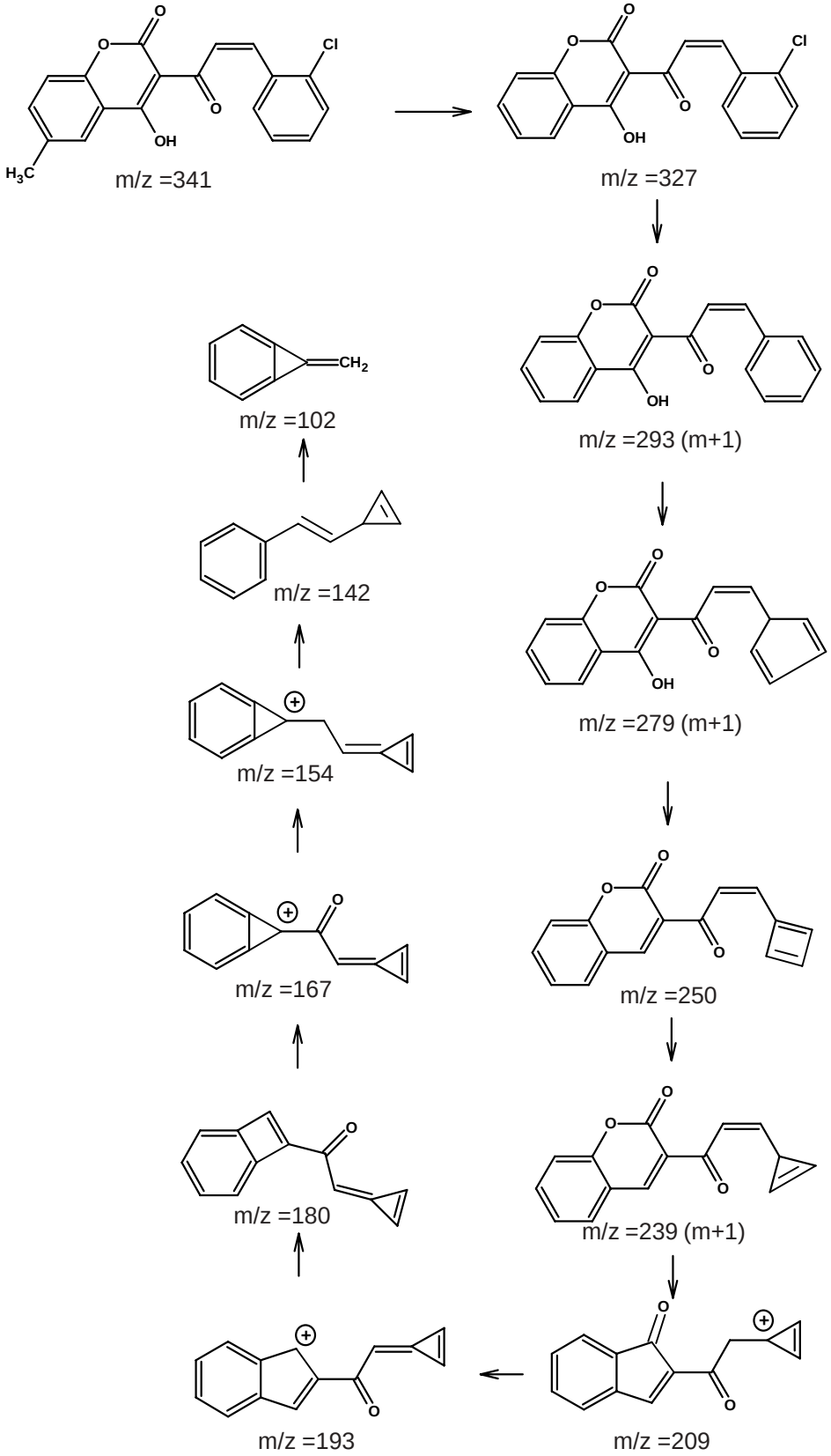
Mass spectral analysis of 3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-BX)

Possible fregmentation pathways is shown below.



Mass spectral analysis of 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-DY)

Possible fregmentation pathways is shown below.



Mass spectral analysis of 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-EY)

Possible fregmentation pathways is shown below.

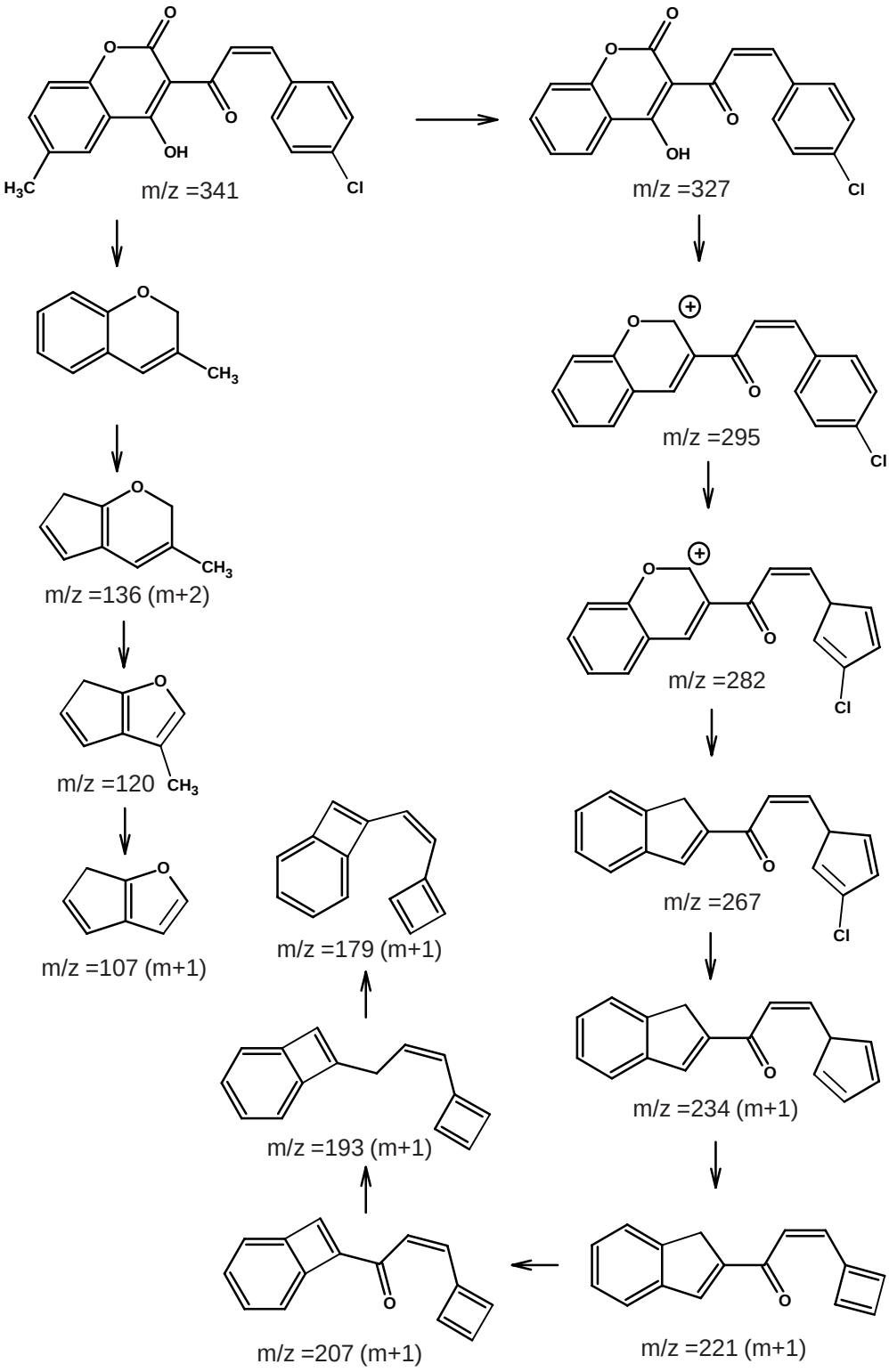
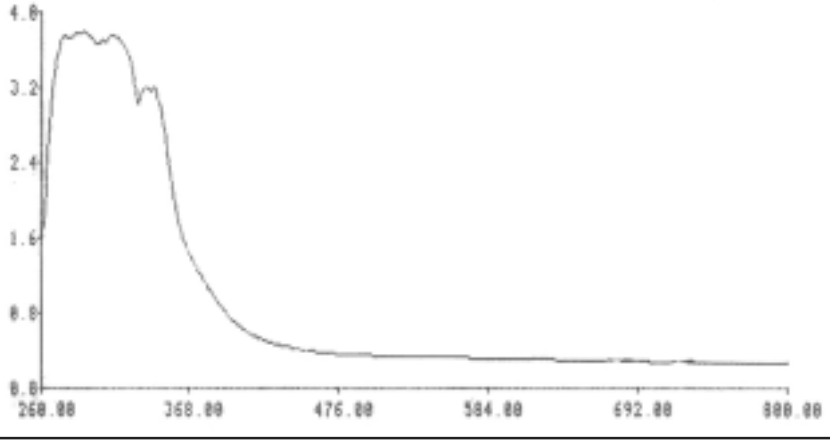


Fig. - 1A
ABSORPTION SPECTRA OF THE LIGANDS

(Chal AX)



(Chal BX)

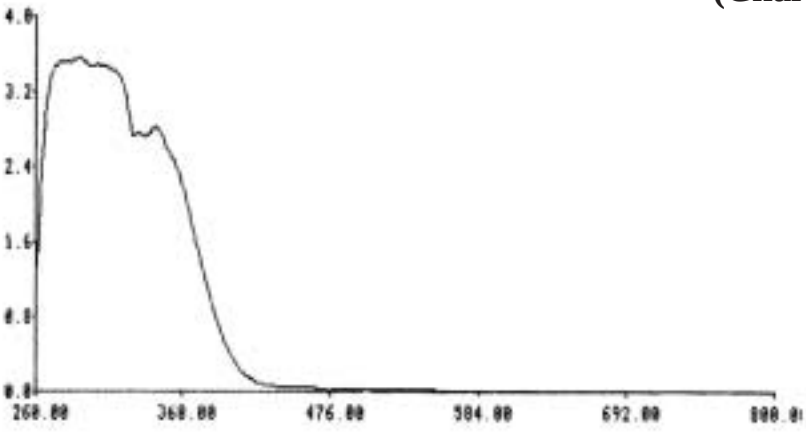
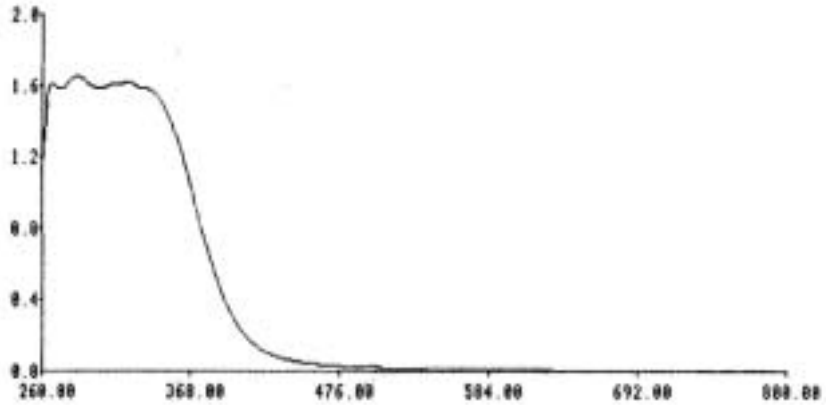


Fig. - 1B
ABSORPTION SPECTRA OF THE LIGANDS

(Chal DY)



(Chal EY)

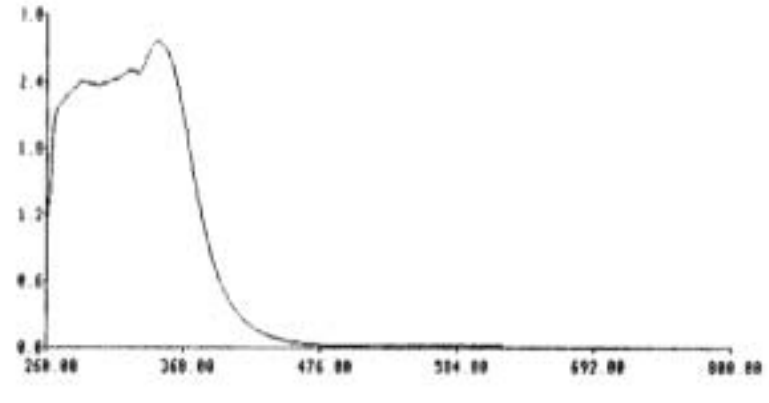


Fig. 2A
NMR SPECTRA OF (Chal - AX)

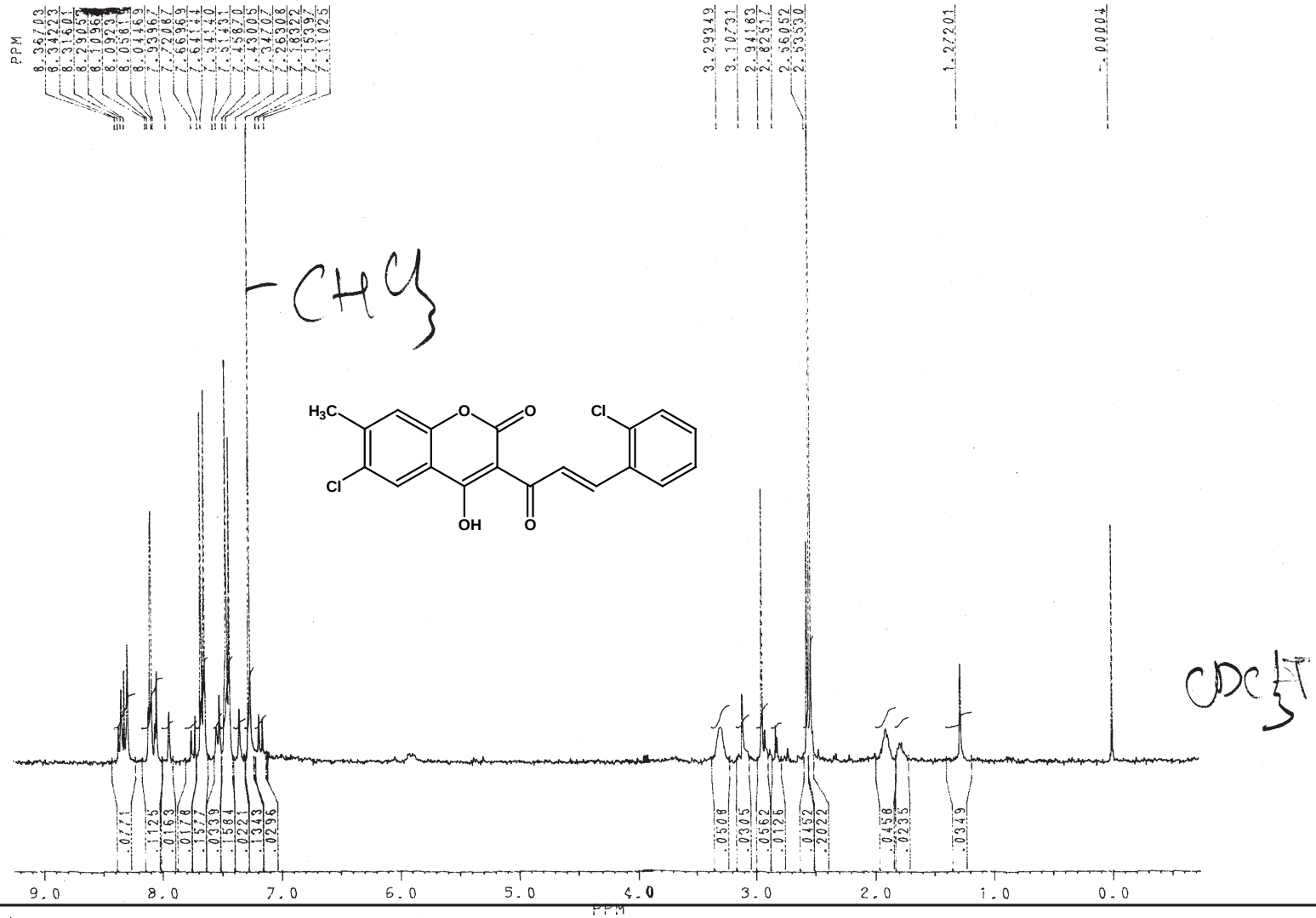
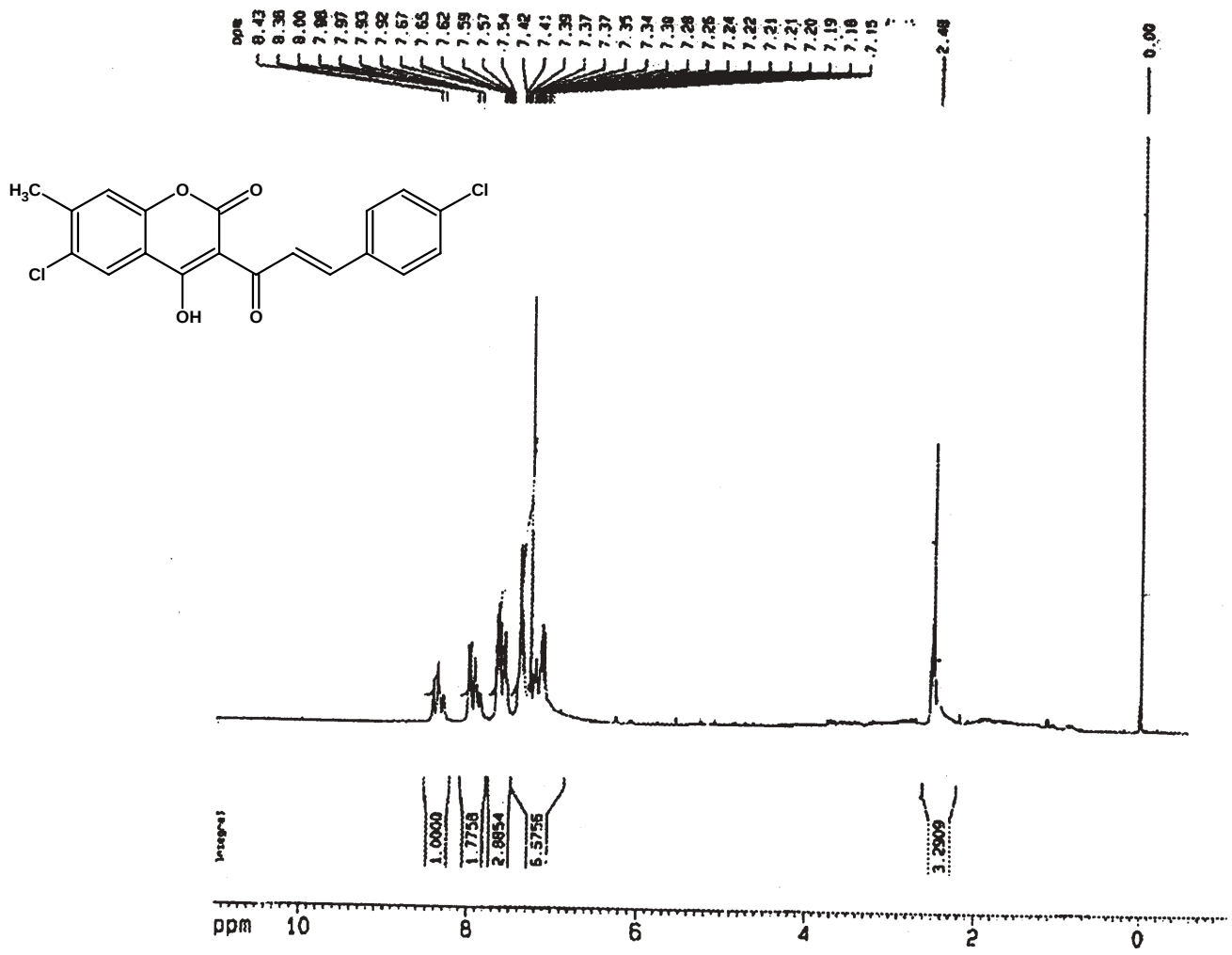


Fig. 2B
NMR SPECTRA OF (Chal - BX)



CDCl3

Fig. 2D

NMR SPECTRA OF (Chal - DY)

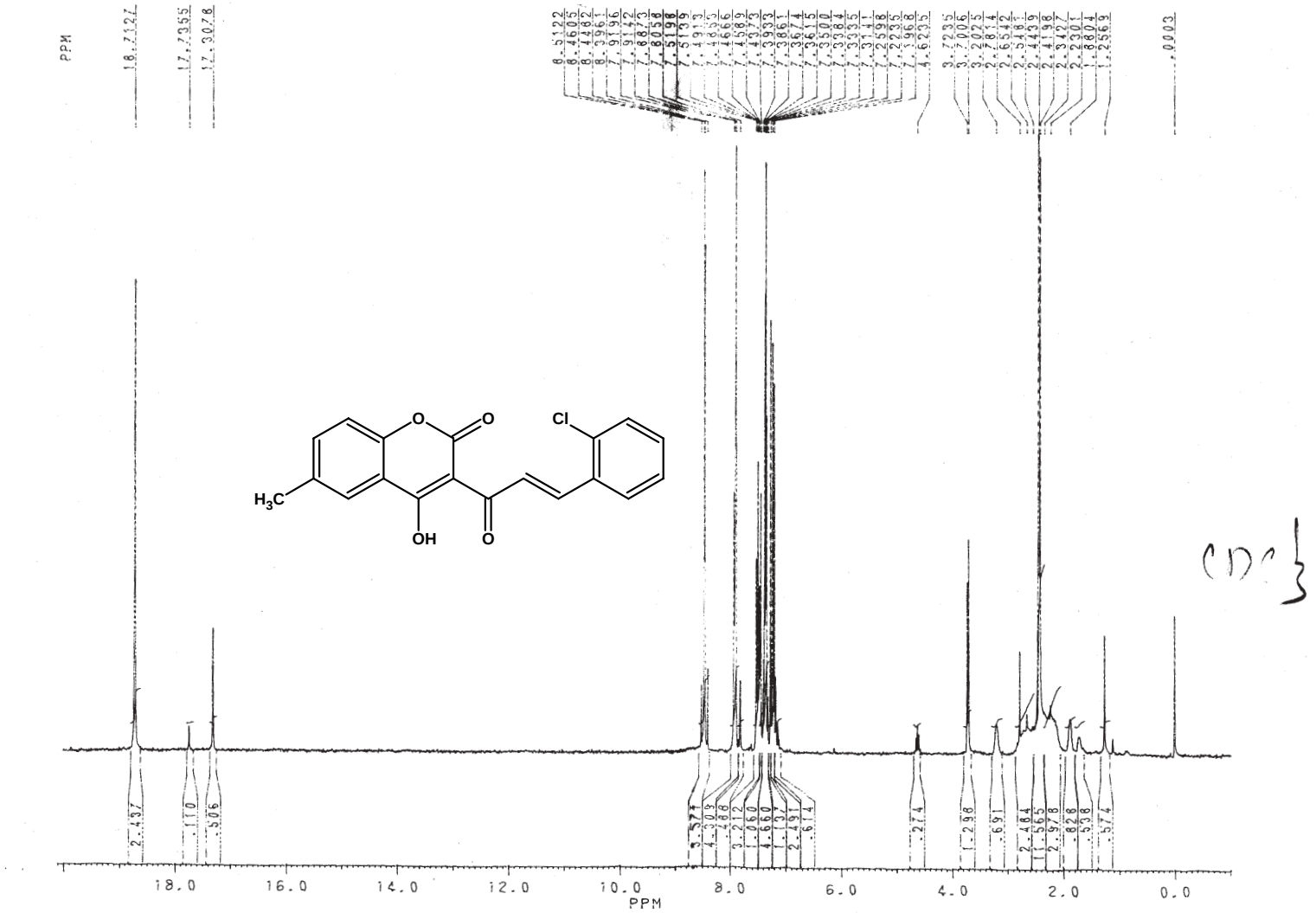


Fig. 2E
NMR SPECTRA OF (Chal - EY)

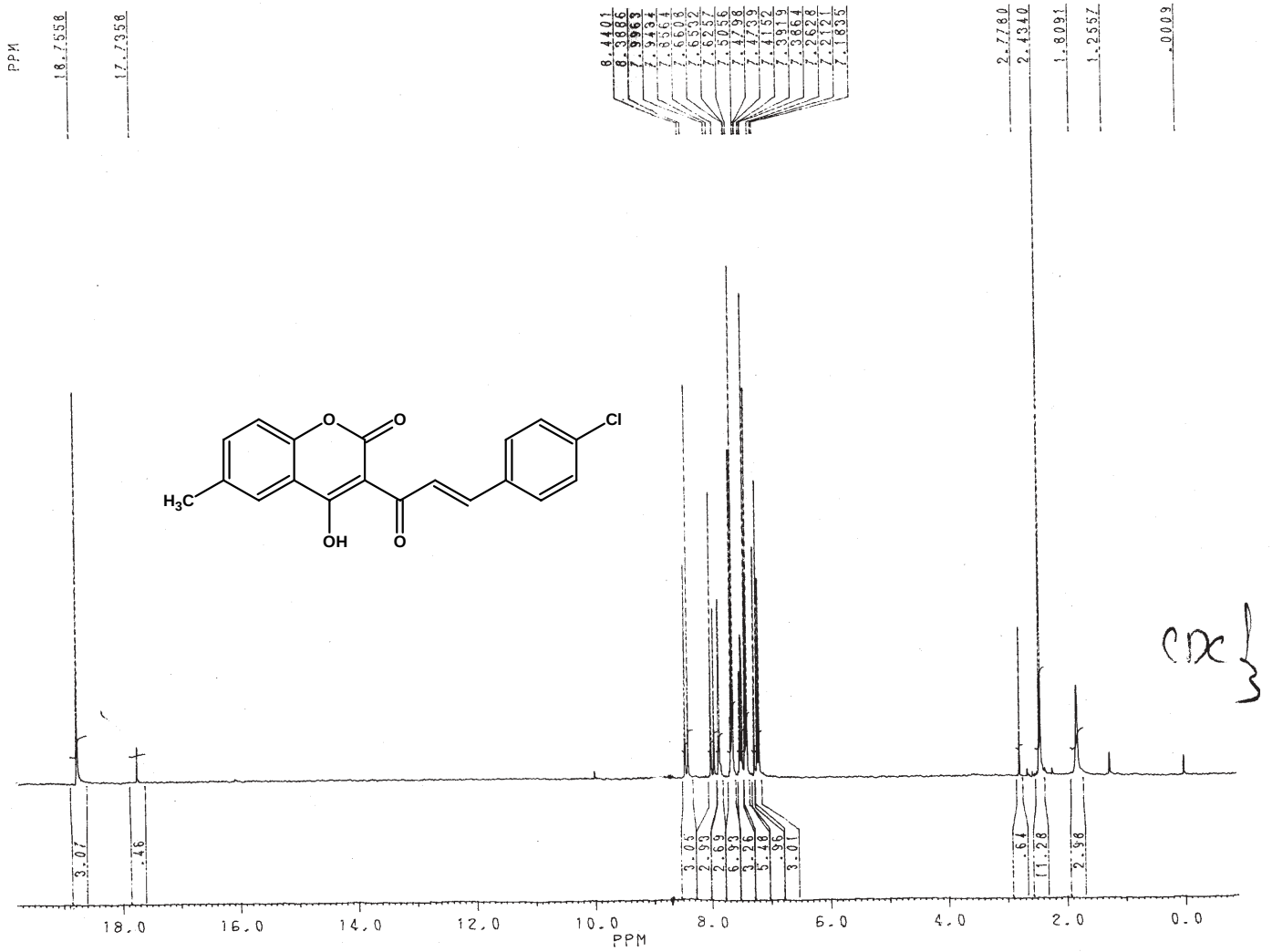
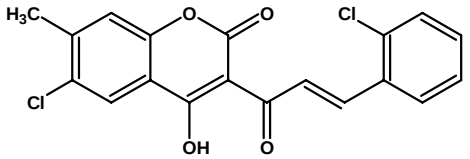


Fig. 3A
IR SPECTRA OF (Chal - AX)



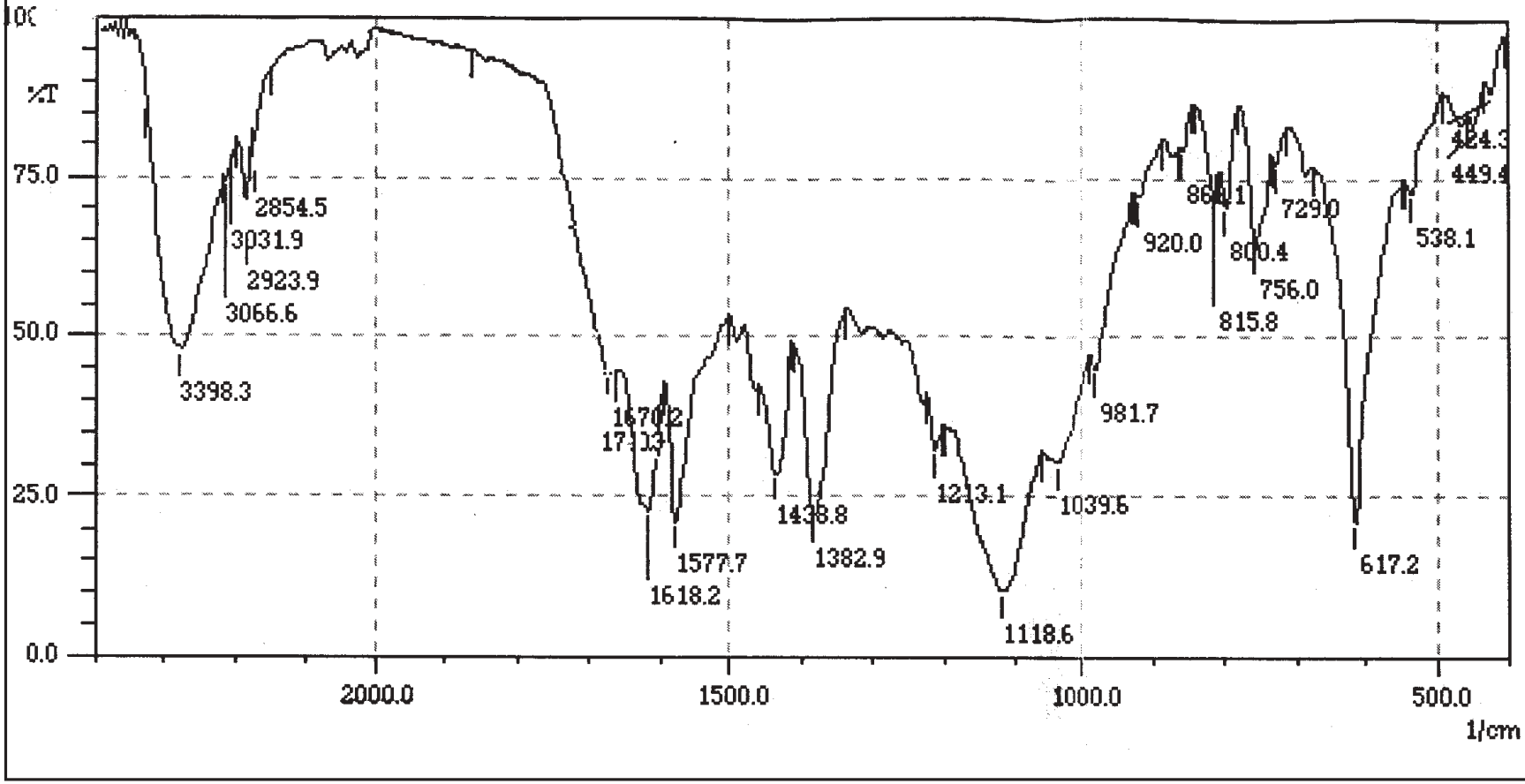
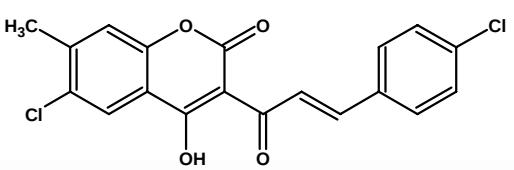


Fig. 3B
IR SPECTRA OF (Chal - BX)



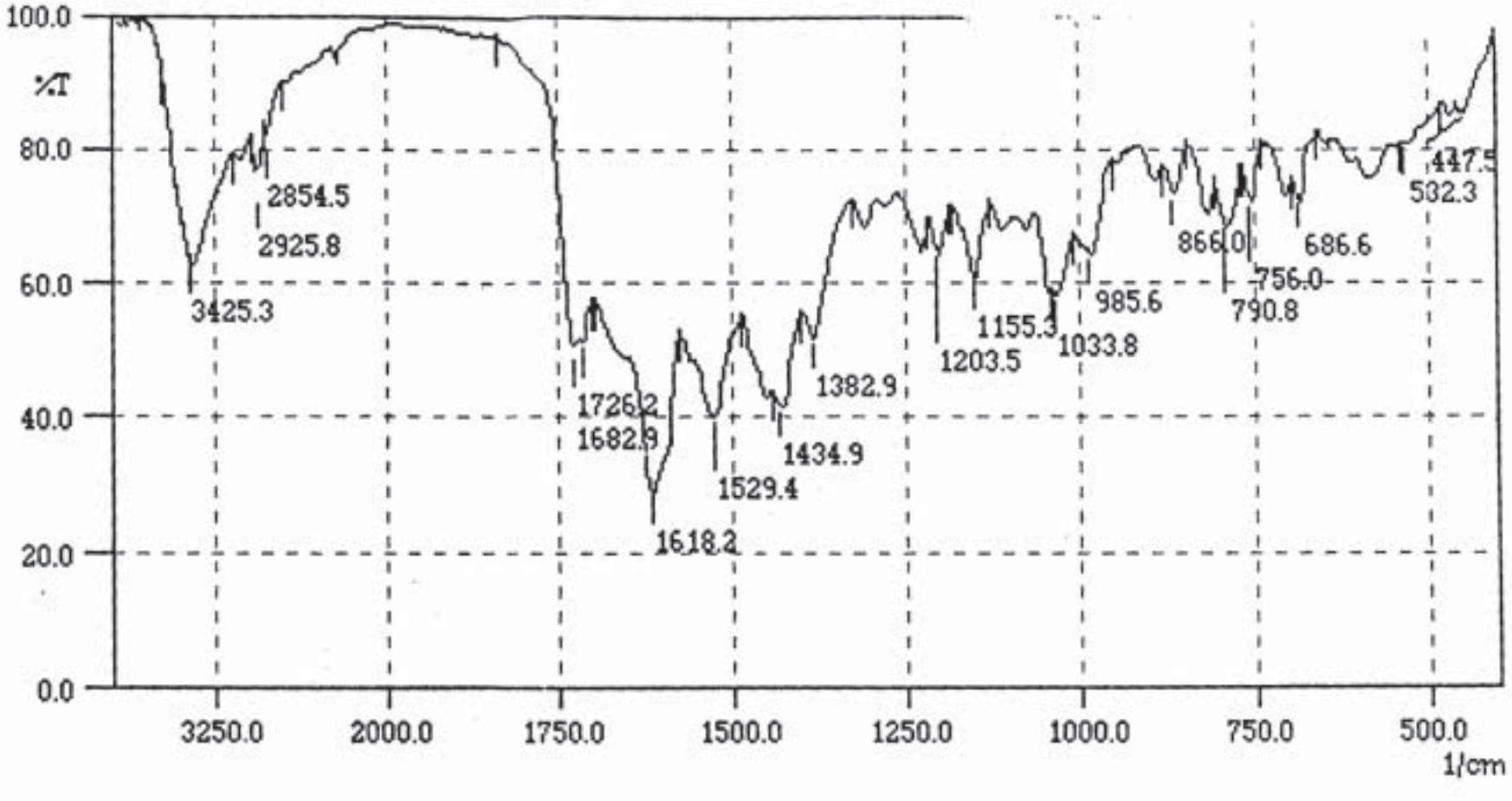
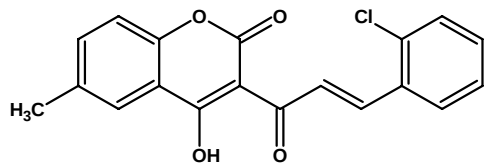


Fig. 3D
IR SPECTRA OF (Chal - DY)



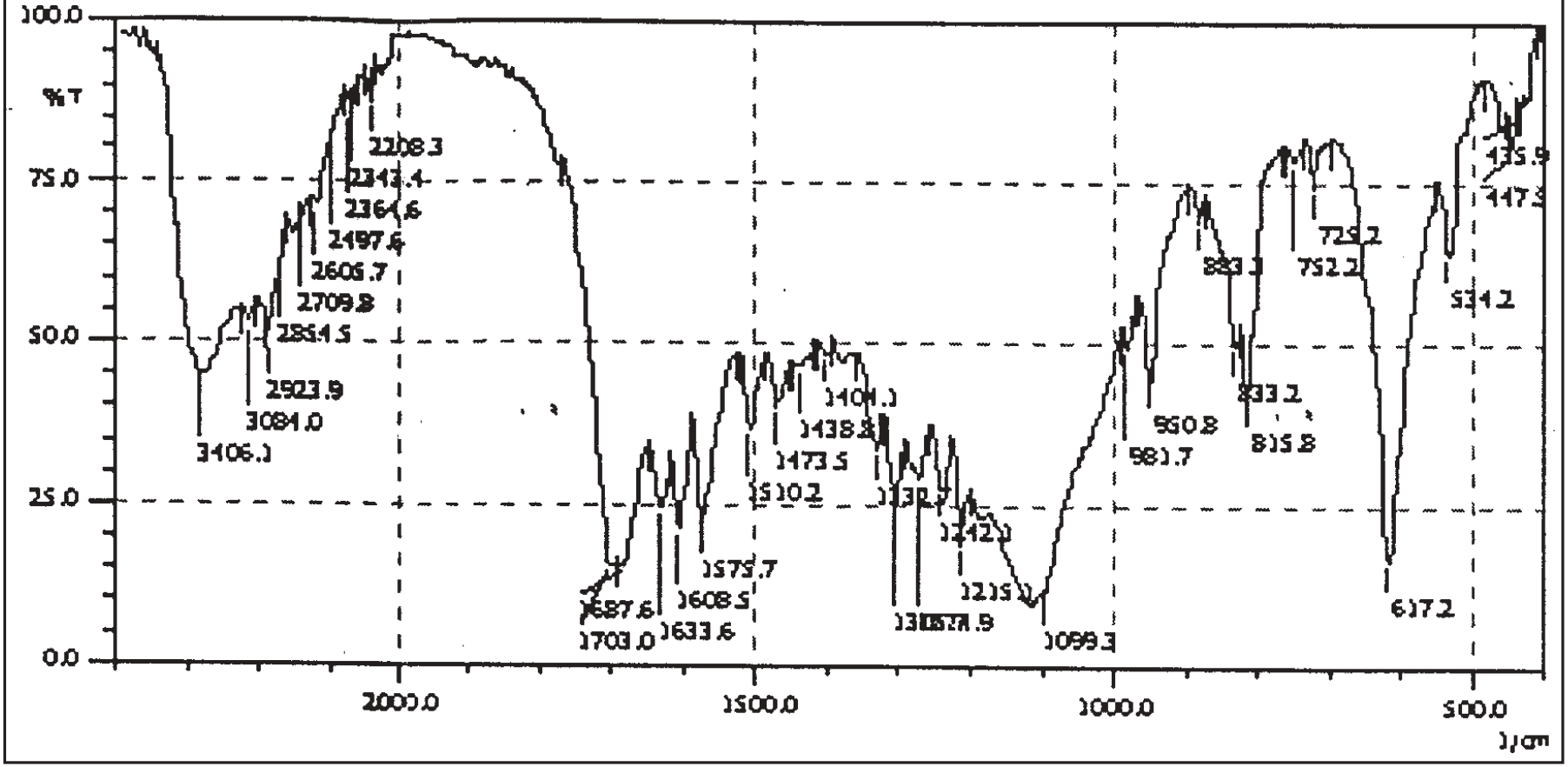
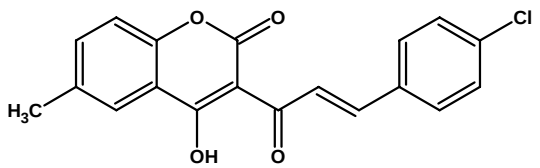


Fig. 3E
IR SPECTRA OF (Chal - EY)



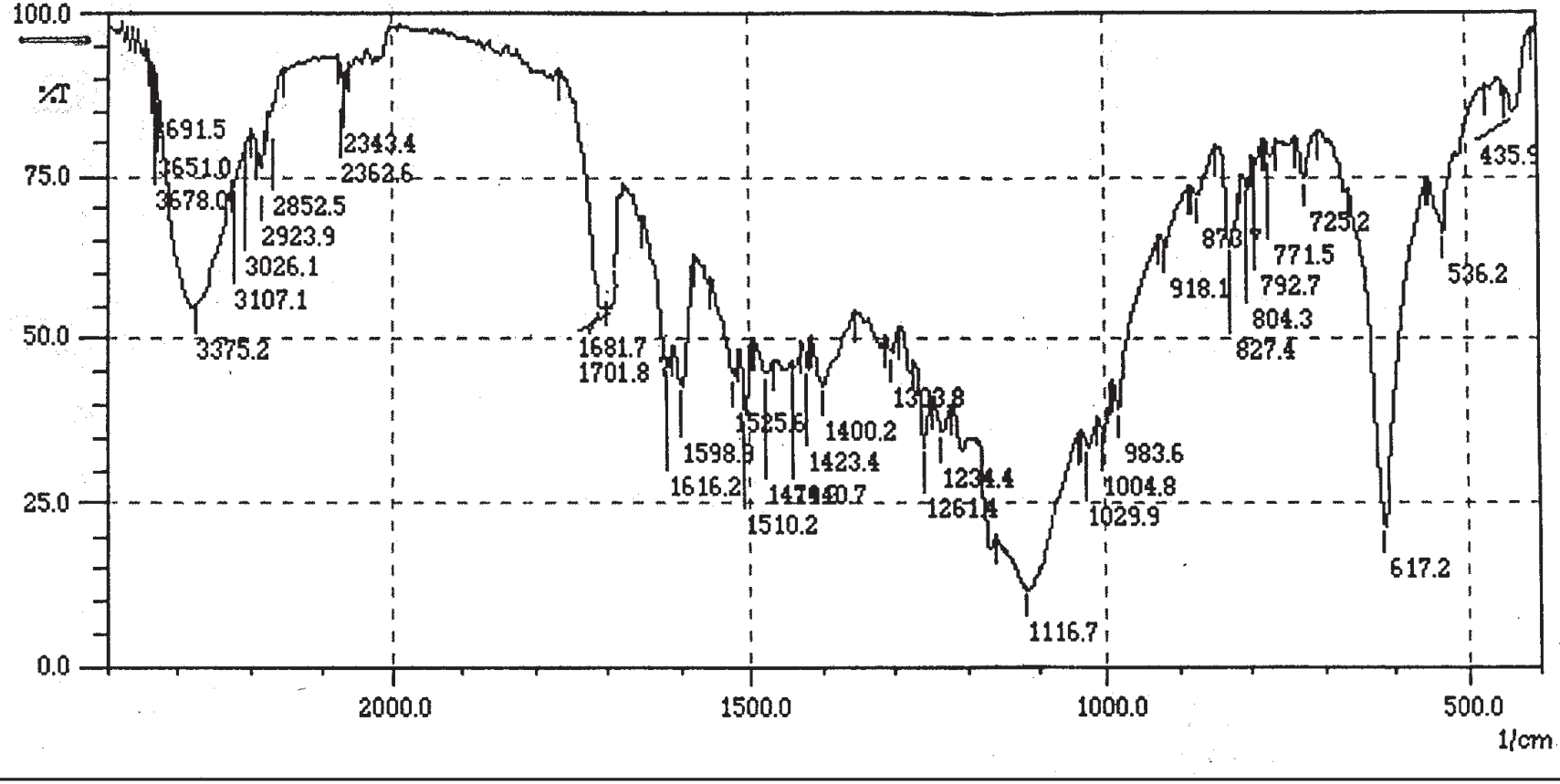
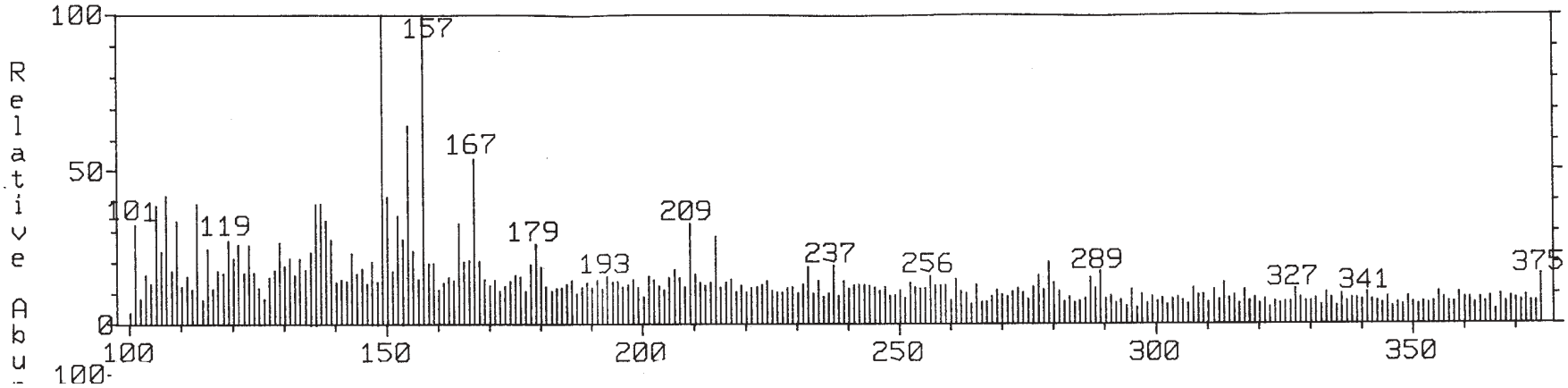


Fig.4A
MASS SPECTRA OF (Chal - AX)

MASS SPECTRUM Data File: 4EFB25M 25-FEB- 4 11:45
SamPle: M-4 DR ANAMIK SHAH RAJKOT #6940
RT 0'36" FAB(Pos.) GC 1.4c BP: m/z 157.0000 Int. 89.2052 Lv 0.00
Scan# (4 to 5)



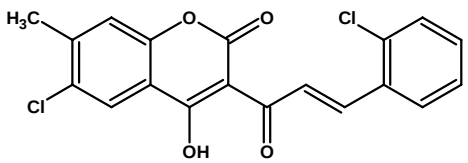
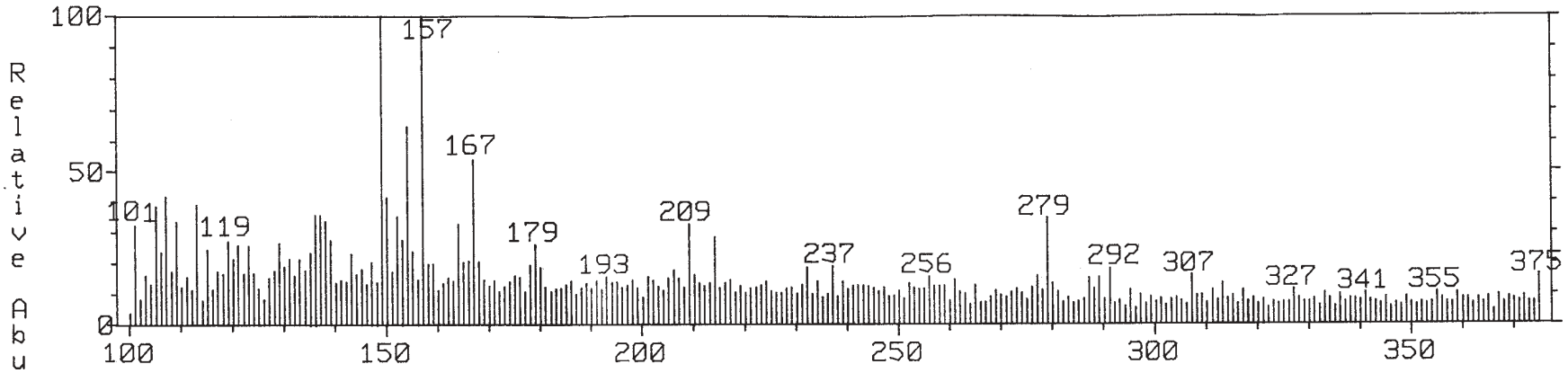


Fig.4B
MASS SPECTRA OF (Chal - BX)

MASS SPECTRUM Data File: 4EFB25M 25-FEB- 4 11:45
Sample: M-11DR ANAMIK SHAH RAJKOT #6940
RT 0'36" FAB(Pos.) GC 1.4c BP: m/z 157.0000 Int. 89.2052 Lv 0.00
Scan# (4 to 5)



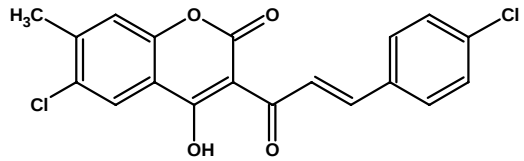
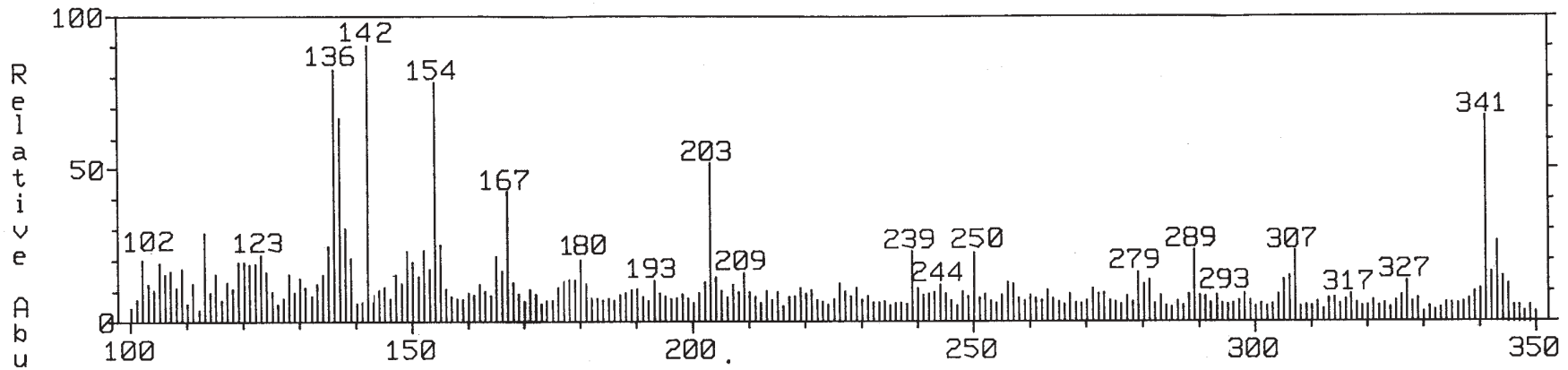


Fig.4D
MASS SPECTRA OF (Chal - DY)

MASS SPECTRUM Data File: 4EFB25K 25-FEB- 4 11:30
SamPle: M-2 DR ANAMIK SHAH RAJKOT #6940
RT 0'24" FAB(Pos.) GC 1.4c BP: m/z 142.0000 Int. 5.1968 Lv 0.00
Scan# (3 to 4)



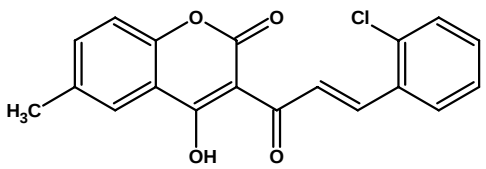
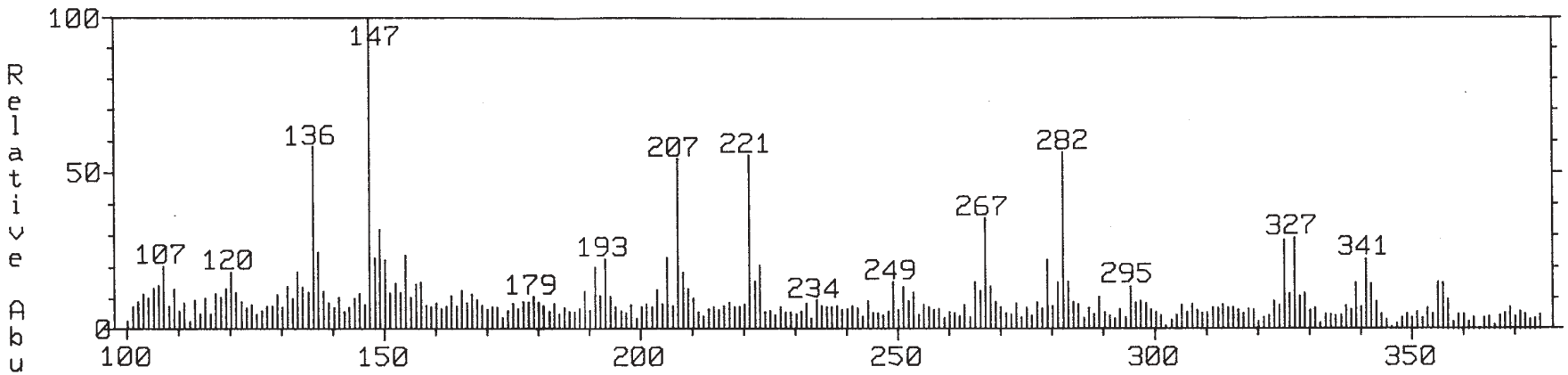


Fig.4E
MASS SPECTRA OF (Chal - EY)

MASS SPECTRUM Data File: 4EFB25N 25-FEB- 4 11:52
Sample: M-10 DR ANAMIK SHAH,RAJKOT #6940
RT 0'12" FAB(Pos.) GC 1.4c BP: m/z 147.0000 Int. 20.9192 Lv 0.00
Scan# (1 to 3)



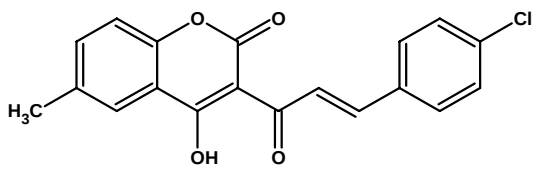
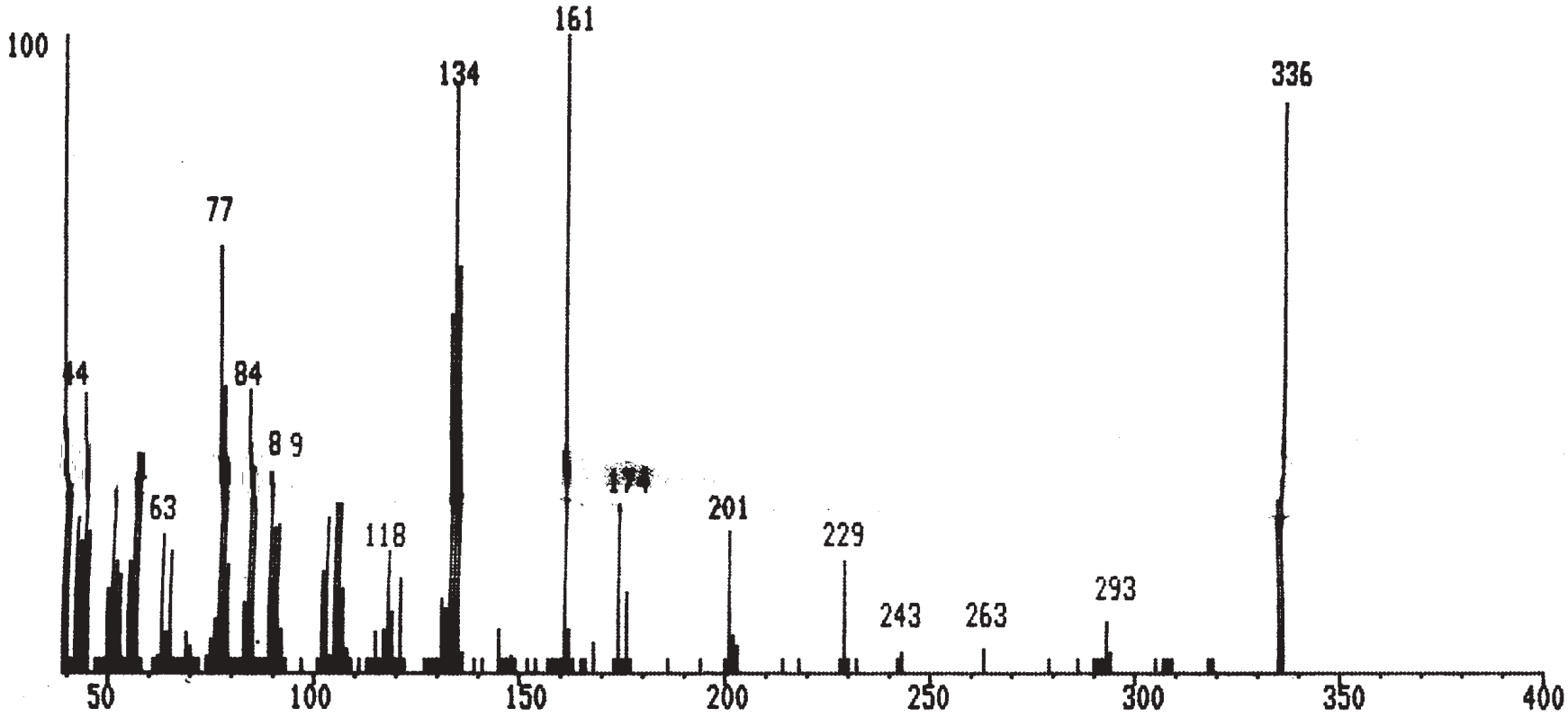


Fig.4F
MASS SPECTRA OF (Chal - FY)



CHAPTER - 2

SYNTHESIS AND ANALYTICAL STUDY OF COPPER COMPLEXES

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SYNTHESIS AND ANALYTICAL STUDY OF COPPER COMPLEXES.

Experimental

PREPARATION OF STANDARD SOLUTIONS:

Cupric chloride ($CuCl_2.2H_2O$):

Cupric chloride (A.R., B.D.H. 17.005g., 0.1M) was dissolved in distilled water, acidified with hydrochloric acid (A.R.) and make it to 1 lit., to get a decimolar solution. It was standardized with 0.1M EDTA solution.

Procedure:

Take 25ml. of cupric chloride solution diluted to 50ml., 5ml. con. ammonia solution to make it alkaline and 5 drops fast sulphon black F indicator was added. It was titrated with standard EDTA solution, until the colour change from blue to dark green solution. The strength of the copper solution was calculated using the relation.

$$1.0ml., 0.1\ M, EDTA = 6.35\ mg.\ Cu^{+2}$$

Sensitivity of the reagent for copper.

The sensitivity test was carried out with the standard cupric chloride solution. The cupric chloride solution (pH 10.7, 0.1M, 0.0063g./ml., 1ml.) was progressively diluted distilled water and treated with ammonium hydroxide to get the pH required. Warm to 60^oC and a few drops of the reagent solution were added. It was found that the precipitates are obtained up to 0.01M concentration of Cu^{+2} ions and turbidity up to 0.005M. and beyond that it was difficult to judge the mode of reaction with an unaided eye.

[A] Synthesis of bis 3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one [$Cu(C_{19}H_{10}O_4Cl_2)_2$]:

Copper chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide was added to get the pH between 10.5-11.0. It was refluxed with excess of alcoholic solution of 3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one [Chal - AX (0.1M)] on a water bath for half an hour when dark purple blue precepitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 300^{o}C.

Conductivity Measurement:

The conductance data for co-ordination compounds provides unimportance experimental evidence in determining the nature of co-ordination compound (whether ionic or covalent).

The conductivity of copper complex was determined using Thoshniwal Conductivity Bridge since the solubility of the complex is less in common organic solvents. It was dissolved in DMF and conductivity was measured.

Conductivity of the DMF along was measured and solution of the complex in DMF with different concentration was measured.

The molar conductivity was calculated using the formula.

$$\textbf{Molecular conductivity} = \frac{1000 \times K}{C}$$

Where, K = Conductivity of the solution of the complex in DMF.

C = Concentration of the complex.

The result is presented in Table – II page 84. The low conductivity confirms the copper complex is non-ionic in nature.

Molecular Weight Determination:

Because of the less solubility of the complex under study in common organic solvent the molecular weight of Bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper (II) complex was determined by Rast's Camphor method.

Rast's Method:

About 50 mg. of the complex was weighted in a test-tube. About 500mg. of the camphor was added and weighed again. The test-tube was sealed completely and heated on water-bath until it becomes a homogeneous mixture. After cooling, the melting point of the mixture was determined by using Backmann thermometer. Difference between the melting point of camphor and of the mixture gave the depression of the melting point of pure camphor caused by addition of the complex. The molecular weight was calculated by using the formula.

$$M = \frac{K \times w \times 1000}{t \times W}$$

Where,

K = Molecular depression constant

w = Weight of complex

W = Weight of camphor

t = Depression of the melting point

The result is presented in Table – II on page 85.

Elemental Analysis:

This involved the estimation of copper, carbon and hydrogen present in the complex. For copper estimation a known weight of complex was broken down in sixty percent A.R. perchloric acid on heating till a clear solution was obtained, it was transferred to 250 ml. measuring flask and the total volume was made to 250 ml by adding required amount of distilled water. From this solution copper was estimated gravimetrically as CuO[1] as well as complexometrically with EDTA. Carbon and hydrogen were estimated[2] on Coolman C-H analyzer. The result are described in Table-II on page 84.

Absorption Spectra of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex:

The compounds or ions containing transition metal exhibit a great range of colours of varying intensity. These colours arise from the characteristic absorption in the visible part of the electro magnetic spectrum. The characteristics visible absorption spectra of the complex usually arise due to electronic transition in the d-orbitals of the metal ions and therefore they are known as *d-d spectra*. The d-orbitals in **Oh** or $\mathbf{D_4h}$ symmetry are of type g and hence these electronic transitions amongst d-orbitals are **Laport-Forbidden transitions** and hence are of low intensity but they are allowed by spin selection rule. The organic part of the ligand shows characteristic absorption maxima in UV region. From spectral studies information in collected regarding the properties of the metal complexes as well as the effect of different substitutions in the ligand molecule. The copper complex of [Chal-AX] known weight dissolved in alcohol and thus alcoholic solution of known concentration was prepared.

Absorption spectra of copper complex of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex was taken using Backmann Spectrophotometer. Their optical density at different

wavelengths were recorded. The results are summarized in Tabel - I on page 83. The nature of absorption curves are shown in Fig.-6A on page 123.

E.S.R spectra of Bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper (II) complex:

Electron spin resonance[3-5] phenomenon in which electromagnetic radiation of microwave-frequency is absorbed by molecules or ions containing one or more electrons with unpaired spins under the influence of a magnetic field. Such compounds possessing unpaired electron exhibit bulk paramagnetism. This phenomenon is also referred to as electron paramagnetic resonance. These chemical species may be atoms, ions, molecules or molecular fragments having an odd number of electrons. The bulk susceptibility and electron spin resonance play complementary roles in exposing the structure of co-ordination complexes.

When electron is introduced[6] in a uniform magnetic field of strength H, the electron magnet dipole will process, about the axis of the field. Analogues to NMR, the larmour frequency of procession "W" is given by,

$$W = yH \qquad \text{---———-———(1)}$$

Where, y = gyromagnetic ratio.

The magnetic energy of interaction, "E" is given as.....

$$E = \mu s.H.\cos\theta \qquad \text{---————————(2)}$$

Where "θ" is angle between the axis of dipole and field interaction and "μs" is the magnetic dipole – moment (θ having only certain definite values).

The resonance condition of unpaired electron is given under.

Let μH be the component of the μs in the direction of the field so that

$$\cos\theta = \mu H / \mu s \qquad \text{————————(3)}$$

$$\mu H = \mu s.\cos\theta \qquad \text{————————(4)}$$

E = -μH.H and μH is given by

$$\mu H = -g.\beta.Ms \qquad \text{————————(5)}$$

Where, β is electronic Bohr magneton and Ms is the magnetic spin quantum number having value +1/2 or –1/2.

$$E = -(-g.\beta.Ms).H \qquad \text{-————(6)}$$

$$= g.\beta.Ms.H$$

For a spin of ½, the electron has a lower energy state (-1/2 gβH) and higher energy state (+1/2gβH). In the absence of field, the two states corresponding to +1/2 have the same energy and are said to be degenerate. The difference in energies for the electromagnetic radiation of frequency to which satisfies the resonance condition is,

$$E_2 - E_1 = H.\ \mu(1/2\ g\beta H) - (-1/2\ g\beta H) \qquad \text{----————(7)}$$

$$E_2 - E_1 = g\beta H \qquad \text{-————(8)}$$

For a free electron (g = 2.0023) the frequency of the radiation absorbed from equation (ΔE = gβH) is ....

$$Y = (2.0023)\ (9.2732 \times 10^{-21})\ H / 6.627 \times 10^{-27} \qquad \text{————(9)}$$

$$Y = 2.082 \times 10^{6}\ .\ H.C. / sec \qquad \text{————(10)}$$

Thus, when magnetic field of 3000 gauss is used the absorption frequency is 8.4×10^{9} C/sec, which falls in the microwave region of the electromagnetic spectrum.

In a magnetic field, the electron spin magnetic moment does not all occupy the lowest energy level. By the Boltzmann distribution law the ration of the nucleus n_1 and n_2 of the electron in the upper and lower energy states, respectively, given by....

$$n_1 / n_2 = e^{-\Delta E / 2KT} \qquad \text{————(11)}$$

Where, ΔE is the energy difference between the two levels and K is the Boltzmann constant. Since ΔE is give by the equation.

$$\Delta E = g.\beta.H \qquad \text{--————(12)}$$

$$n_1 / n_2 = e^{-g\beta H/2KT} \qquad \text{---—--—(13)}$$

The smaller the value of n_1/n_2 higher is the absorption probability and

hence sensitivity, therefore, increases steeply with the field strength.

For obtaining an ESR spectrum, the sample containing an unpaired electron is placed in a constant magnetic field and simultaneously irradiated by n ratio frequency field (in microwave range) that produces a rotating field perpendicular to the fixed magnetic field direction.

The resonance frequency satisfies the relation,

$$\mu = g\beta H\lambda h \text{ c/ sec.} \qquad \text{————(14)}$$

Energy absorbed from the rotating field at resonance cause the electron spins to slip from the lower energy level to the higher energy level. The absorption of the energy is measured electrically and recorded on a chart.

ESR experiments[7-9] are performed by detecting the amount of energy absorbed therefore, in order to improve the sensitivity of detection, we want to have as many electrons in the lower state as possible this is achieved by either reducing the temperature or increasing the field strength or both, most commonly used techniques being recording of the spectra at liquid nitrogen temperature.

ESR spectroscopy provides a powerful[10] tool for the study of chemical species with unpaired electrons. It gives information not only on the presence and number of such electrons as can be often studied by measurements of paramagnetism but also on the distribution of unpaired electrons in the molecules.

ESR spectra of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper (II) complex were recorded by ESR laboratory, IIT Madras at room temperature. ESR spectra of copper complex of Chal-AX are presented in fig. 5A on page 86.

Magnetic Susceptibility:

Application of magnetic measurement to the study of complex compound was due to pauling[11,12] and nearly all recent work on the subject have been interpreted in pauling's term. The use of the magnetic susceptibility measurements in the study of the complexes arises from the fact that electrons used in covalent bond formations are necessarily paired and so contribute nothing to the magnetic moment of the molecule. It is possible to compute the number of the unpaired electronics in a complex because the moment is often gives by $\mu eff = [n(n + 2)]^{1/2}$. Where, 'n' is the number of unpaired electrons.

The paramagnetic part of the susceptibility of a transition group elements is approximately represented by *"spin only"* formula using the relations.....

$$\chi_m = \frac{NB^2[4S(S+1)]}{3KT}$$

$$\mu_{eff} = [4S(S+1)^{1/2}]BM$$

$$= [n(n+2)^{1/2}]BM$$

where, χ_m = Molecular susceptibility

N = Avogrado's number

B = Bohr magnetone

S = The quantum specifying the total spin angular moment of the ions.

n = Number of the unpaired electrons.

μ_{eff} = Effective moment

T = Absolute temperature

K = Boltzman constant.

Gouy Balance Method:

χ (magnetic susceptibility) can be measured by number of methods. But Gouy's method[13] is being used by number of workers. It has the advantage the apparatus is simple and robust and can be used to measure a wide range of susceptibility. It consists essentially of suspending a uniform rod of the specimen in a non-homogeneous magnetic field and measuring, by a conventional weighting technique, the force exerted on it.

If the field gradient over an element of volume of the specimen $\partial H/\partial_1$ than the force F exerted is

$$\partial F = (K_1 - K_2)\, V.H.\partial H/\partial_1$$

Where, K_1 and K_2 are the susceptibilities per unit volume of the specimen and of the displaced medium respectively. Integration over the whole length of the specimen from $H = H_1$ at zero length $H = H_0$ at length = ℓ

$$F = \frac{(K_1 - K_2)\,.\,V.(H_1^2 - H_0^2)}{2\ell}$$

If F is dynes is replaced by w.e where W is in gram and $(H_1^2 - H_0^2)$ by H^2, then,

$$K_1 = K_2 + \frac{2\ell gw}{H^2V}$$

$$K_1 = \chi P = m/V.C$$

Where, m is total weight of the specimen, m/V is the density of the specimen of volume V.

$$\chi = \left\{\frac{K_2V + \frac{2g\ell w}{H^2}}{m}\right\}$$

$$= \frac{\alpha + \beta F^1}{m}$$

χ = K_1.V/m; substituting the value of K_1 we have,

where, α = constant for displaced air (K_2V)

= 0.029 X specimen volume X 10^{-6} C.G.S.

(volume susceptibility of air K V = $0.029 + 10^{-6}$ C.G.S.

β = Tube calibration constant ($2\ell^2 / H^2$)

F' = Real force of the magnetic field acting on the specimen

m = weight of the specimen

α is given by the product of the volume susceptibility of air (i.e. known = + 0.029 X 10^{-6} C.G.S.) and volume occupied by the specimen.

Theβ is given by the expression

$$\beta = \frac{2\ell}{H_2^1 - H_0^2} \quad \text{or} \quad 2\ell/H^2$$

It required determination of 'ℓ' the length of the specimen column, H_1 and H_0, the respective field strength at the two ends of the specimen tube. It is difficult to determine these quantities with a great accuracy. In practice therefore, β is determined by using a standard substance of known magnetic susceptibility. We have glass distilled water, as standard substance to determine β.

After determining α and the specific susceptibility χ and molecular susceptibility χ_m was calculated on applying Pascal's diamagnetic correction data the χ_m corrected (χ_M^{corr}.) was as obtained and the effective magnetic moment was calculated as....

$$\mu_{eff} = 2.84\sqrt{\mu_M^{corr}.T}$$

The μeff was also calculated using the formula....

$$\mu_{eff} = \sqrt{n(n+2)}$$

where 'n' is the number of unpaired electron present in the complex.

For the determination of magnetic susceptibility of copper complex, the pyrex glass tube was thoroughly cleaned with chromic acid, washed several times with distilled water and finally with acetone and dried. It was suspended with the pan

of Gouy's balance so that its bottom position remained between the gap of the two poles of electromagnet one centimeter apart. The tube was weighted with and without magnetic field, several times till constant weight was obtained. The differences between the two-weights (i) without magnetic field and (ii) with the magnetic field gave a measure of the force acting on the tube due to the magnetic field. The tube was filled with the specimen (complex) under investigation up to the fixed mark. The complex was grinded to fine powdered form and filled in such a manner that there was no air gap remained in the column of the specimen. It was cleaned from outside just to remove off any adhered particle and was suspended as before to the balance. It was weighed with and without magnetic field. The process was repeated till constant values are obtained. The tube was taken out, evacuated, washed and dried. It was then filled with distilled water and weighed with and without magnetic field. The same method was adopted for weighing the empty tube.

Pascal Constant:

	All values X 10^{-6} g. atom		
H	-2.93	Cl	-20.10
C	-6.00	Br	-30.60
N	-5.57	I	-44.60
N *(Ring)*	-4.61	S	-15.00
N *(Mono amine)*	-1.54	F	-26.30
N *(Di amine-imine)*	-2.11	Fe(II)	-10.40
O	-4.61	As(II)	-20.90
O *(Ketone)*	+1.73	Cu(II)	+11.00
O_2 *(Carboxylate)*	-7.95	Co(II)	-12.80
F	-6.30	Ni(II)	-12.80

Constitutive Corrections

All values X 10^{-6} g. atom

C *(In ring)*	-0.24	C=N	+8.15
C *(Shared by ring)*	-3.07	C-N	+0.80
C=C bond	-5.50	N=N	+1.80
C-C bond	+0.80	N=O	+1.70

Observations:

Weight of the empty tube without field = 10.3816 g.

Weight of the empty tube with field = 10.3720 g.

Weight of the tube + water without field = 11.7068 g.

Weight of the empty tube + water with field = 11.7000 g.

Volume of the specimen or water column:

m = [Weight of tube + Water without field] – [Weight of the empty tube without field]

= 11.7068 g. - 10.3816 g.

= 1.3252 g.

Mass of the water = 1.3252 g.

Volume of the water = 1.3252 g.

Density of the water = 1.00 g./ml.

Since the complex was filled up to the same mark up to which there was water level, hence volume of the specimen is equal to the volume of water in the tube = 1.3252 g.

CALCULATION OF α - [Constant for displaced air]:

α = Volume susceptibility of air x Volume of specimen

= 0.029×10^{-6} C.G.S. x 1.3252

= 0.0384×10^{-6} C.G.S.

CALCULATION OF β :

$$\beta = \frac{\chi\omega \times m - \alpha}{F^1}$$

$\chi\omega$ = Susceptibility of water = 0.72×10^{-6} C.G.S.

m = Mass of water = 1.3252 g.

F^1 = The real force of magnetic field action on water.

F^1 = $\Delta\omega - \delta$ (mg.)

$\Delta\omega$ = (Weight of the tube + water with field
- (Weight of the tube + water without field)

= 11.7005 g. - 11.7068 g.

= -0.0063 g.

= -6.30 mg.

δ = (Weight of the empty tube with field)
- (Weight of the empty tube without field)

= 10.3720 g. - 10.3816 g.

= -0.0096 g.

= -9.60 mg.

F^1 = $\Delta\omega - \delta$

= -6.30 - (-9.60)

= 3.30

$$\beta = \frac{\mu\omega \times m - \alpha}{F^1}$$

$$= \frac{[-0.72 \times 10^{-6} \times 1.3252] - [0.0384 \times 10^{-6}]}{-3.30}$$

$$= \frac{[-0.954 \times 10^{-6}] - [0.0384 \times 10^{-6}]}{-3.30}$$

$$= \frac{+0.9925 \times 10^{-6}}{+3.30}$$

$\beta = 0.3008 \times 10^{-6}$ C.G.S.

The magnetic susceptibility measurement of Chal AX Copper(II) presented in the Table-III on page 85.

[B] Synthesis of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] Copper(II) complex $[Cu(C_{19}H_{10}O_4Cl_2)_2]$:

Copper chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide with excess to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of 3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-BX(20 ml., 0.01M)] on a water bath for half an hour when *light green* precipitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{O}C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complexes do not show clear melting point. It gets char at temperature above 280^{O}C.

Conductivity Measurement:

The conductivity of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 84.

Molecular Weight Determination:

The molecular weight of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex was determined by Rast's

camphor method. The method is described on page 66. The result is presented in Table-II on page 84.

Elemental Analysis:

Estimation of copper, carbon and hydrogen present in the bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex were determined using the method as described on page 67.The result is described in Table-II on page 84.

Absorption Spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex

Absorption spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex was taken using Backmann spectrophotometer. Their optical density at different wavelengths were recorded. The results are summarized in table-I on page 83. The nature of absorption curve is shown in fig 6B on page 124.

E.S.R spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex

ESR spectra of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] copper(II) complex was recorded by ESR laboratory, IIT Madras at room temperature. ESR spectra of copper complex of Chal-BX are presented in fig5B on page 87.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[Chal BX] copper(II) complex was measured by Gouy-balance method. The method is described on page 72. The result is presented in Table-III. on page 85.

[D] Synthesis of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex: [Cu($C_{19}H_{11}O_4Cl)_2$]

Copper chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide with excess to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex [Chal-DY, (20ml, 0.1M)] on a water bath for half an hour when yellow precipitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o} C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 84.

Molecular Weight Determination:

The molecular weight of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex was determined by Rast's camphor method. The method is described on page 66. The result is presented in Table-II on page 84.

Elemental Analysis:

Estimation of copper, carbon and hydrogen present in the bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 84.

Absorptions Spectra of Bis [3-[{3-(2'-chlorophenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex

Absorption Spectra of Bis [3-[{3-(2'-chlorophenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths was recorded. The results of absorption curves are shown in table-I on page 83. The nature of absorption curve is shown in fig6D on page 125.

E.S.R spectra of Bis [3-[{3-(2'-chlorophenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex

ESR spectra of Bis [3-[{3-(2'-chlorophenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] complex were recorded by ESR laboratory, IIT Madras at room temperature. ESR spectra of copper complex of [Chal-DY] is presented in fig 5D on page 88.

Magnetic Susceptibility:

Magnetic susceptibility of Bis [3-[{3-(2'-chlorophenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex was measured by Gouy-balance Method. The method is descried on page 71. The result is presented in Table-III. on page 85.

[E] Synthesis of Bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex: $[Cu(C_{19}H_{11}O_4Cl)_2]$

Copper chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] [Chal-EY (10.1M)] on a water bath for half an hour when *green* precipitates of copper complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o} C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complexes do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 84.

Molecular Weight Determination:

The molecular weight of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex was determined by Rast's camphor method. The method is described on page 66. The result is described in Table-II on Page 84.

Elemental Analysis:

Estimation of copper, carbon and hydrogen present in the bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex were determined using the method as described on page 67.The result as described in Table-II on page 84.

Absorption Spectra of Bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex

Absorption Spectra of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex was taken using Backmann spectrophotometer. Their optical density at different wavelengths was recorded. The results of absorption curves are shown in table-I on page 83. The nature of absorption curve is shown in fig6E on page 126 .

E.S.R spectra of Bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper(II) complex:

ESR spectra of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex were recorded by ESR laboratory, IIT Madras at room temperature. ESR spectra of copper complex of (Chal-EY) are presented in fig 5E on page 89.

Magnetic Susceptibility:

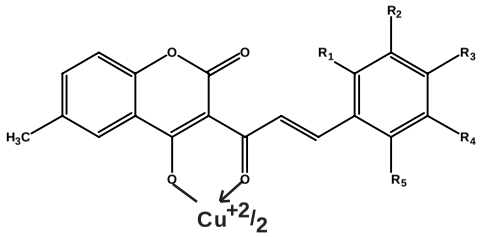
Magnetic Susceptibility of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] copper (II) complex was measured by Gouy-balance Method. The method is described on page 71. the result is presented in Table-III . on page 85.

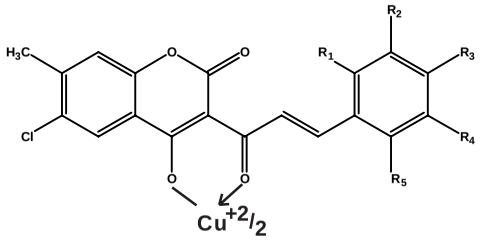
TABLE-I

Absorption maximum (λ max) and log ε of metal complexes.

SR. NO.	METAL COMPLEXES	λ max. (nm)	log ε
1	Cu (Chal-AX)$_2$	299.6	3.434
		280.4	3.438
		479.4	0.043
2	Cu (Chal-BX)$_2$	344.0	2.980
		301.4	3.289
		292.1	3.394
		263.0	3.401
		491.3	0.311
		602.0	0.079
3	Cu (Chal-DY)$_2$	343.8	1.192
		307.8	1.148
		280.5	1.227
		548.2	0.072
		742.5	0.041
4	Cu (Chal-EY)$_2$	350.5	2.803
		341.0	2.868
		320.4	2.913
		281.2	2.901
		598.2	0.035

TABLE-II
ANALYTICAL DATA OF METAL CHELATES





Where R_1, R_2 and R_3 are described on page 33, 34

Sr.No.	NAME OF METAL CHELATES	MOLECULAR FORMULA	MOLECULAR WEIGHT	% OF CARBON		% OF HYDROGEN		% OF COPPER		CONDUC' Mohs
				CAL	FOUND	CAL	FOUND	CAL	FOUND	
1	$Cu(Chal\ AX)_2$	$Cu(C_{19}H_{12}O_4Cl2)_2$	809.54	50.92	50.89	1.41	1.38	11.23	11.20	8.3
2	$Cu(Chal\ BX)_2$	$Cu(C_{19}H_{12}O_4Cl2)_2$	809.54	51.73	51.70	1.51	1.51	9.78	9.74	7.8
3	$Cu(Chal\ DY)_2$	$Cu(C_{19}H_{13}O_4Cl)_2$	741.54	50.69	50.66	1.22	1.19	7.06	7.03	8.0
4	$Cu(Chal\ EY)_2$	$Cu(C_{19}H_{13}O_4Cl)_2$	741.54	56.33	56.30	1.36	1.33	7.85	7.83	7.9

TABLE-III
MAGNETIC SUSCEPTIBILITY OF METAL CHELATES

* **Current : 6 Amps.**
* **α = 0.0384 x 10^{-6} C.G.S.**
* **β = 0.3008 x 10^{-6} C.G.S.**
* **Temp. = 300^0 K**

Sr.	Molecular Formula	Molecular Weight	Amount of Compound in g. (m)	Force of magnetic field 'F' in g.	$\chi = \beta F + \alpha / m$	$\chi M = \chi . M.$ 10^{-6} C.G.S.	$\chi M^{Corr} = \chi . M - M^{Corr}$ 10^{-6}C.G.S.	μeff B.M.
1	$Cu(C_{19}H_{12}O_4Cl2)_2$	809.54	0.3521	2.3785	2.1410	1210.83	1490.23	1.89
2	$Cu(C_{19}H_{12}O_4Cl2)_2$	809.54	0.3715	2.3941	2.0418	3626.25	1636.31	1.99
3	$Cu(C_{19}H_{13}O_4Cl)_2$	741.54	0.4749	2.3153	1.5325	1378.56	1873.50	2.13
4	$Cu(C_{19}H_{13}O_4Cl)_2$	741.54	0.4605	2.3361	1.6093	1302.83	1736.54	2.05

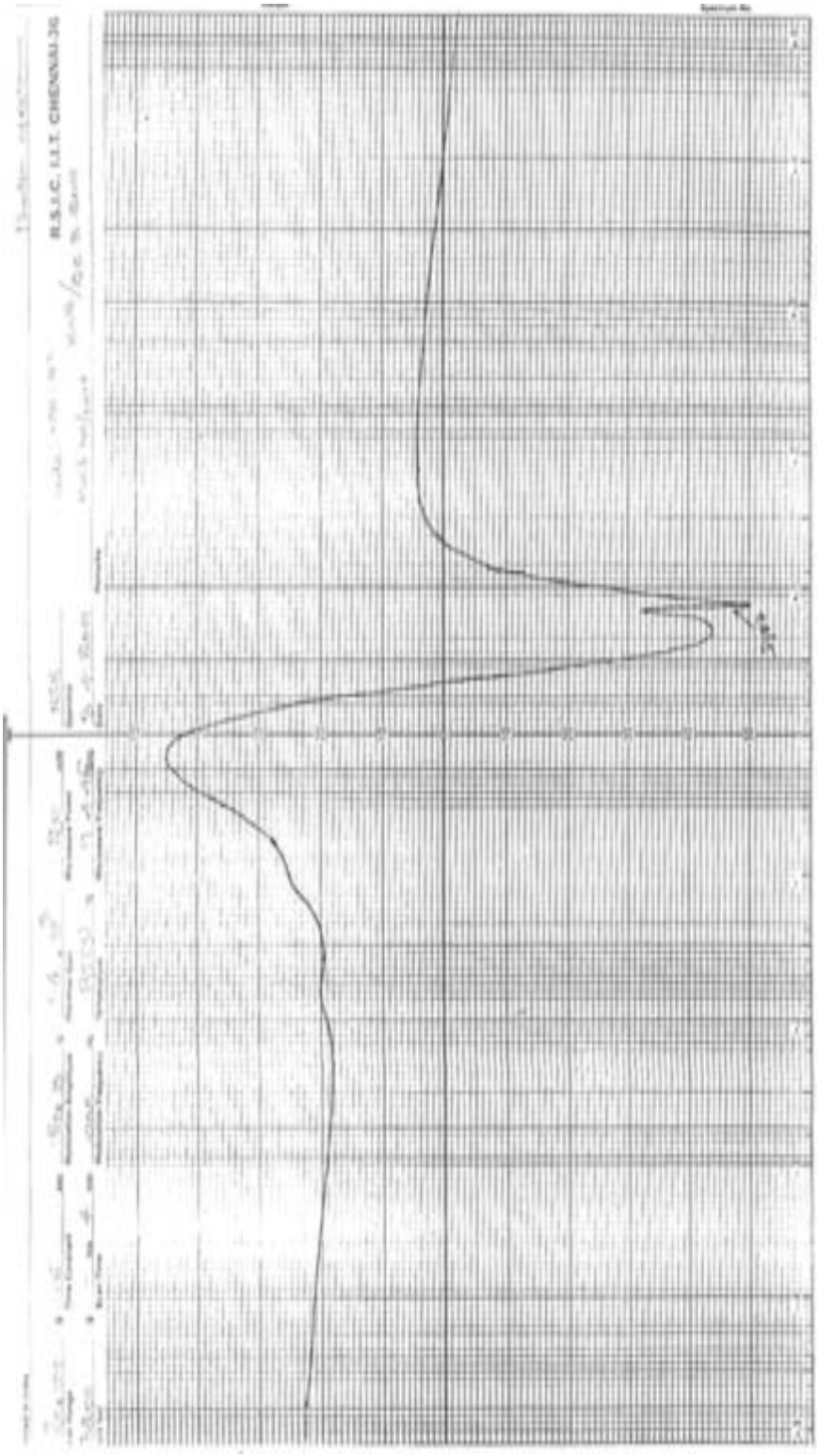


Fig. - 5A
ESR SPECTRA OF $Cu(Chal\ AX)_2$ AT R.T.

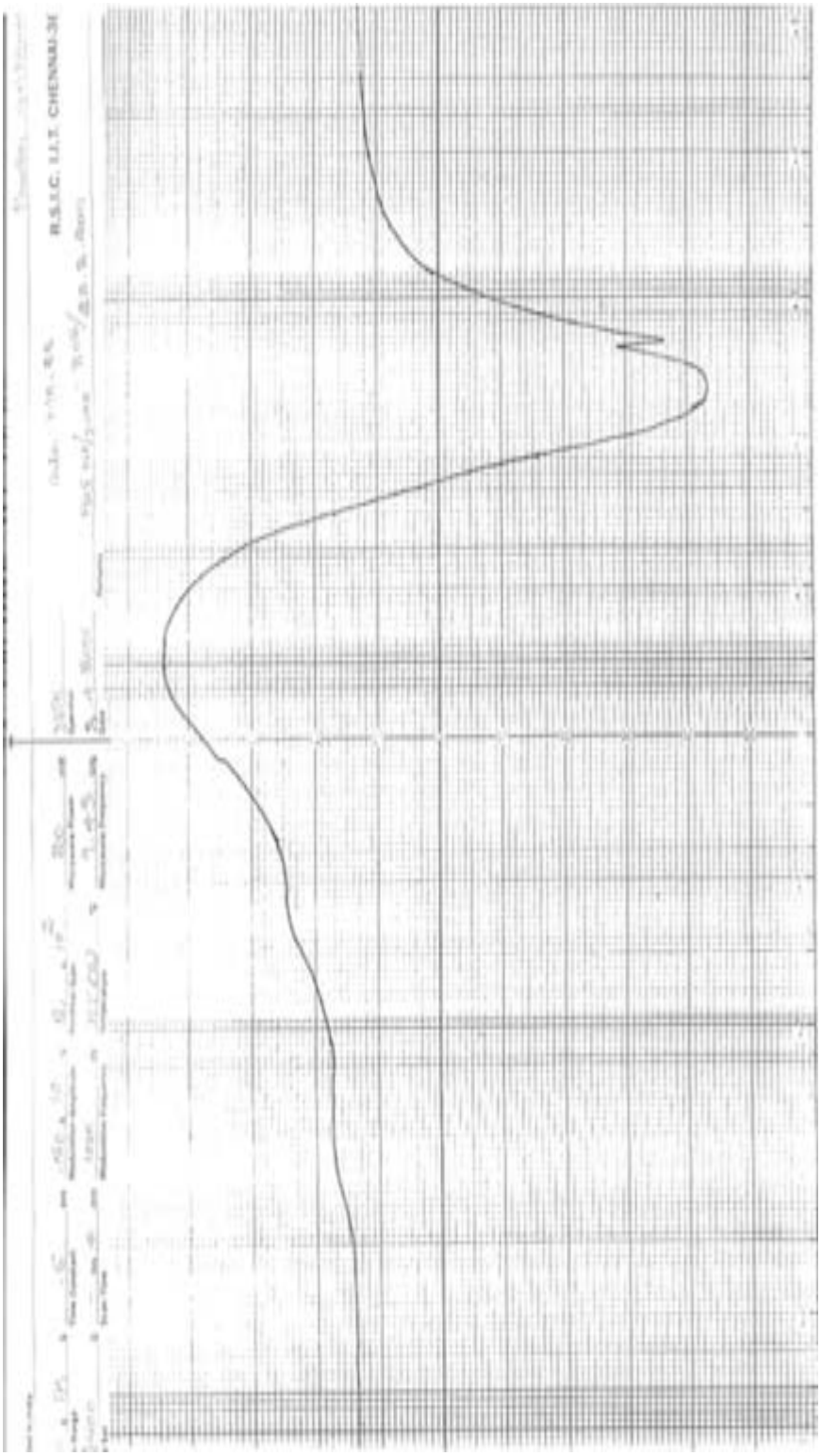


Fig. - 5B
ESR SPECTRA OF $Cu(Chal\ BX)_2$ AT R.T.

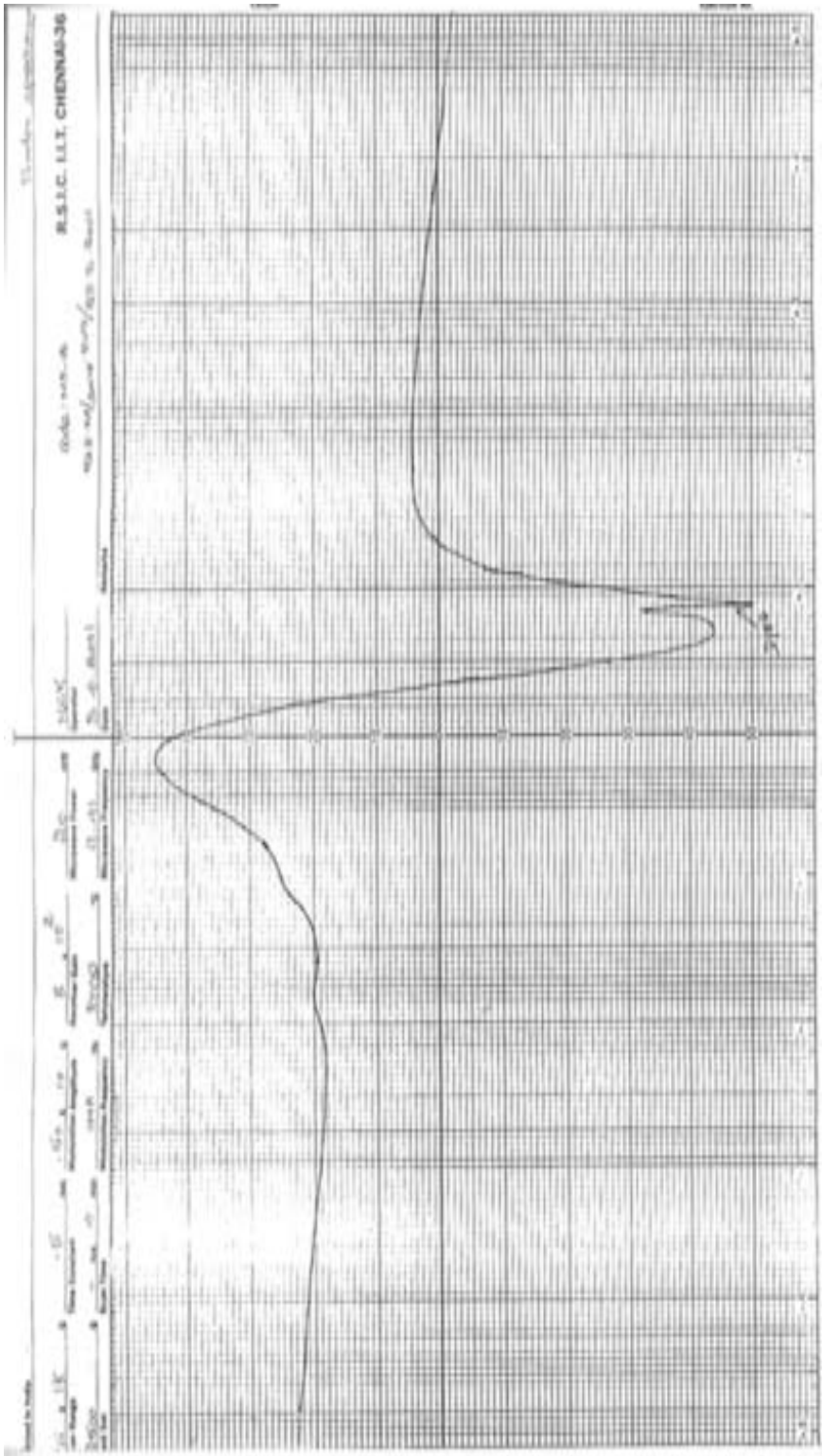


Fig. - 5D
ESR SPECTRA OF $Cu(Chal\ DY)_2$ AT R.T.

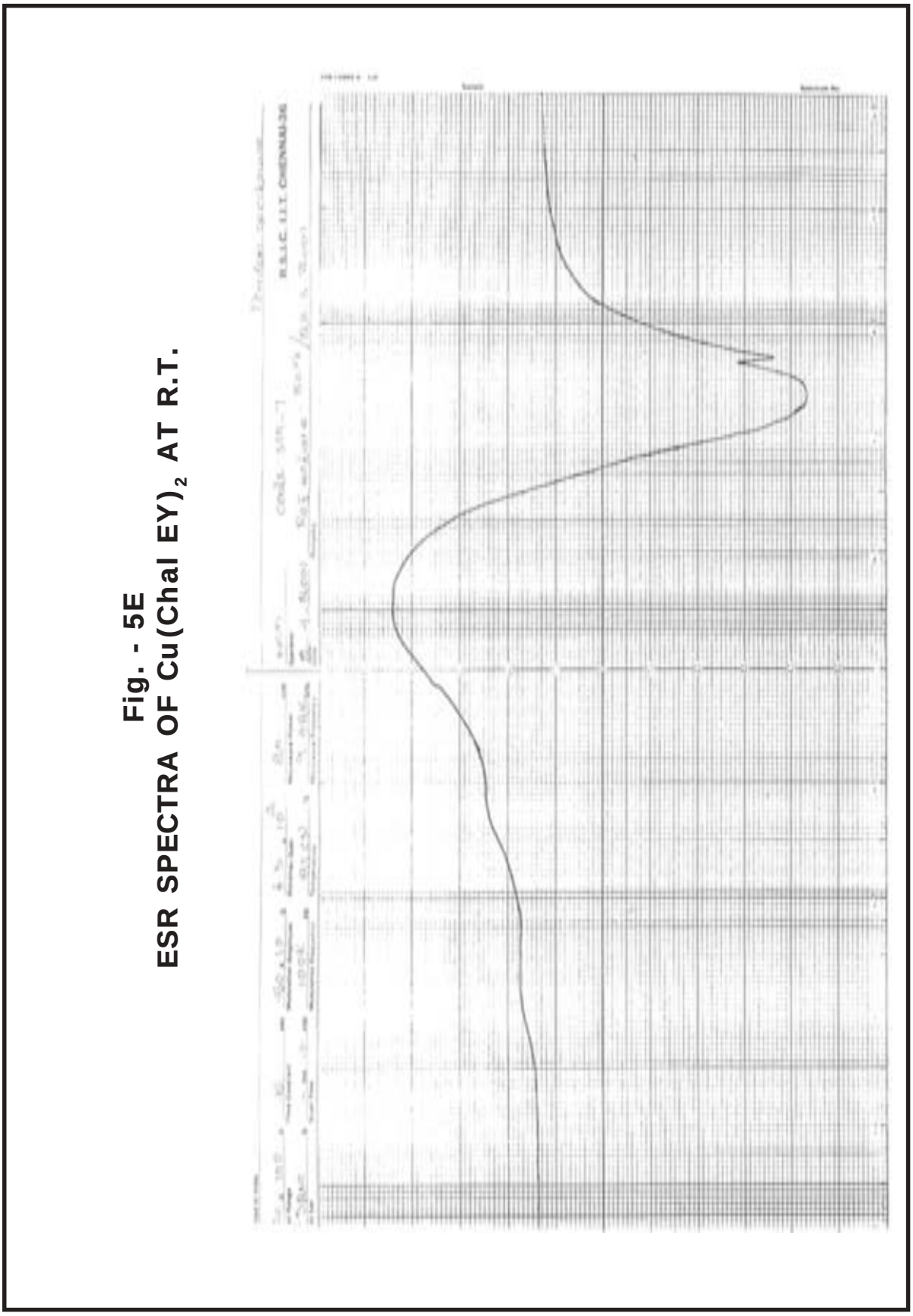


Fig. - 5E
ESR SPECTRA OF $Cu(Chal\ EY)_2$ AT R.T.

CHAPTER - 3

SYNTHESIS AND ANALYTICAL STUDY OF NICKEL COMPLEXES

CHAPTER – 3

SYNTHESIS AND ANALYTICAL STUDY OF NICKEL COMPLEXES:

Experimental

PREPARATION OF STANDARD SOLUTIONS:

Nickel chloride ($NiCl_2.2H_2O$):

Nickel chloride (A.R.,B.D.H.23.763g., 0.1M) was dissolved in distilled water, acidified with hydrochloric acid (A.R.) and made to 1 lit. to get a decimolar solution. It was standardized with 0.1M EDTA solution.

Buffer solutions:

This was prepared as required by mixing equal volume of 1 M ammonium chloride and 1M aqueous ammonia solutions.

Procedure:

Pipette 25ml. of nickel ion solution into a conical flask and diluted the solution to 150 ml. with distilled water. Add about 15 drops of bromopyrogallol red indicator and 10 ml. of buffer solution. Titrate with std. EDTA solution until colour change from blue to clear red.

The strength of the nickel solution was calculated using the relation.

1.0 ml., 0.1M, EDTA = 5.87 mg. Ni^{+2}

[A] Synthesis of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel (II) complex $[Ni(C_{19}H_{10}O_4Cl_2)_2]$:

Nickel chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution

of [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-AX(20 ml, 0.1M)] on a water bath for half an hour when *dark purple blue*-precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 300^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was determined by the method as described in Chapter–2 on page 65. The result is presented in Table – II on page 99.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was determined by Rast's camphor method. The method is described in Chapter – 2 on page 66. The result is presented in the Table – II on page 99.

Elemental Analysis:

This involved the estimation of nickel, carbon and hydrogen present in the bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex were determined using the method as described in Chapter–2 on page 67. the result is presented in the Table – II on page 99.

Absorption Spectra of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex

Absorption Spectra of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was taken using Backmann spectrophotometer. The optical density at different wavelength was recorded. The result are summarized in Table–I on page 98. The nature of absorption curve is shown in fig 6A on page 123.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was measured by Gouy balance method. The method is described in Chapter – 2 on page 71. The result is presented III on page 100.

[B] Synthesis of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel (II) complex $[Ni(C_{19}H_{10}O_4Cl_2)_2]$:

Nickel chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-BX (0.1M)] on a water bath for half an hour when a *coffee black* precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100°C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complexes do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was determined by the method as described in Chapter-2 on page 65. The result is presented in Table-II on page 99.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 99.

Elemental Analysis:

Estimation of nickel, carbon and hydrogen present in the bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] nickel(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 99.

Absorption Spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] Nickel (II) complex :

Absorption spectra of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] Nickel(II) complex was taken using Backmann spectrophotometer. Their optical density at different wavelengths was recorded.

The results of absorption curves are shown in table-I on page 98. The nature of absorption curve is shown in fig 6B on page 124.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] Nickel(II) complex was measured by Gouy-balance Method. The method is descried on page 71. The result is presented in Table-III on page 100.

[D] Synthesis of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel (II) complex : [Ni($C_{19}H_{11}O_4Cl)_2$]

Nickel chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (30g. in 10ml. of water) was a added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex [Chal-DY(10.1M)] on a water bath for half an hour when *light green* precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^oC. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^oC.

Conductivity Measurement:

The conductivity of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was determined by the method as described in chapter-2 on page 65. The result is presented in Table-II on page 99.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 99.

Elemental Analysis:

Estimation of nickel, carbon and hydrogen present in the bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 99.

Absorption Spectra of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel(II) complex

Absorption spectra of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 98. The nature of absorption curve is shown in fig6D on page 125.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was measured by Gouy-balance Method. The method is descried in Chapter-2 on page 71. The result is presented in Table-III on page 100.

[E] Synthesis of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel(II) complex : [Ni($C_{19}H_{11}O_4Cl)_2$]

Nickel chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml. of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] (Chal-EY) (20 ml, 0.1M)]on a water bath for half an hour when *dark green* precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^oC. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^oC.

Conductivity Measurement:

The conductivity of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 99.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 99.

Elemental Analysis:

Estimation of nickel, carbon and hydrogen present in the bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex were determined using the method as described in chapter-2 on page 67. The result as described in Table-II on page 99.

Absorption Spectra of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel(II) complex :

Absorption spectra of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 98. The nature of absorption curve is shown in fig6E on page 126.

Magnetic Susceptibility:

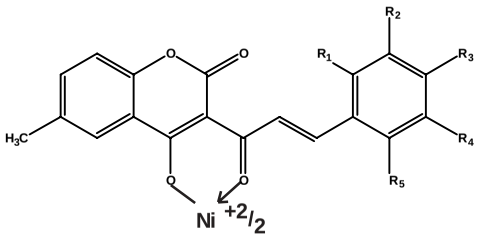
Magnetic Susceptibility of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] nickel(II) complex was measured by Gouy-balance Method. The method is described in Chapter-2 on page 71. The result is presented in Table-III on page 100.

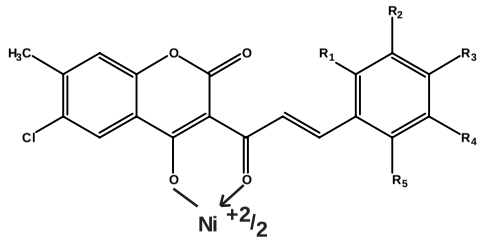
TABLE-I

Absorption maximum (λ max) and log ε of metal complexes.

SR. NO.	METAL COMPLEXES	λ max. (nm)	log ε
1	$Ni(Chal\text{-}AX)_2$	362.2	1.213
		314.5	1.610
		289.1	1.600
		471.2	0.380
		560.1	0.040
2	$Ni(Chal\text{-}BX)_2$	335.8	2.805
		322.3	2.671
3	$Ni(Chal\text{-}DY)_2$	330.4	1.592
		307.6	1.680
		275.3	1.583
		461.2	0.407
		533.5	0.183
4	$Ni(Chal\text{-}EY)_2$	358.3	3.208
		286.5	3.381
		280.2	3.408
		570.1	0.062
		599.5	0.041

TABLE-II
ANALYTICAL DATA OF METAL CHELATES





Where R_1, R_2 and R_3 are described on page 33, 34

Sr. No.	NAME OF METAL CHELATES	MOLECULAR FORMULA	MOLECULAR WEIGHT	% OF CARBON		% OF HYDROGEN		% OF NICKEL		CONDUCTIVITY Mohs cm^2
				CAL	FOUND	CAL	FOUND	CAL	FOUND	
1	Ni(Chal AX)$_2$	Ni($C_{19}H_{12}O_4Cl_2$)$_2$	804.71	51.36	51.33	1.42	1.38	10.47	10.44	8.9
2	Ni(Chal BX)$_2$	Ni($C_{19}H_{12}O_4Cl_2$)$_2$	804.71	52.12	52.08	1.55	1.51	9.10	9.07	9.5
3	Ni(Chal DY)$_2$	Ni($C_{19}H_{13}O_4Cl$)$_2$	736.71	50.97	50.94	1.23	1.20	6.56	6.53	8.7
4	Ni(Chal EY)$_2$	Ni($C_{19}H_{13}O_4Cl$)$_2$	736.71	56.66	56.63	1.37	1.33	7.30	7.27	9.9

TABLE-III
MAGNETIC SUSCEPTIBILITY OF METAL CHELATES

* **Current : 6 Amps.**
* **α = 0.0384 x 10^{-6} C.G.S.**
* **β = 0.3008 x 10^{-6} C.G.S.**
* **Temp. = 300^0 K**

Sr.	Molecular Formula	Molecular Weight	Amount of Compound in g. (m)	Force of magnetic field 'F' in g.	$\chi = \beta F + \alpha / m$	$\chi M = \chi . M . 10^{-6}$ C.G.S.	$\chi M^{Corr} = \chi . M - M^{Corr} 10^{-6}$ C.G.S.	μeff B.M.	N un ele
1	$Ni(C_{19}H_{12}O_4Cl_2)_2$	804.71	0.3612	-2.3822	-2.0901	-1171.97	-892.57	-	Dia
2	$Ni(C_{19}H_{12}O_4Cl_2)_2$	804.71	0.3771	-2.4151	-2.0282	-1307.64	-997.58	-	Dia
3	$Ni(C_{19}H_{13}O_4Cl)_2$	736.71	0.4655	-2.3303	-1.5883	-1421.06	-926.12	-	Dia
4	$Ni(C_{19}H_{13}O_4Cl)_2$	736.71	0.4384	-2.3591	-1.7062	-1373.02	-939.28	-	Dia

CHAPTER - 4

SYNTHESIS AND ANALYTICAL STUDY OF COBALT COMPLEXES

CHAPTER – 4

SYNTHESIS AND ANALYTICAL STUDY OF COBALT COMPLEXES:

Experimental

PREPARATION OF STANDARD SOLUTIONS:

Cobalt chloride ($CoCl_2.2H_2O$):

Cobalt chloride (A.R., B.D.H.23.783g., 0.1M) was dissolved in distilled water, acidified with hydrochloric acid (A.R.) and made to 1 lit. to get a decimolar solution. It was standardized with 0.1M EDTA solution.

Procedure:

Pipette 25ml. of cobalt ion solution in to a conical flask and diluted the solution to 50 ml. with distilled water. Add 3 drops of xylanol orange indicator followed by very diluted sulphuric acid until colour just change from red to yellow. Add powedered hexamine with shaking until the deep red colour is restored (pH ~ 6.0). Warm the solution to about $40^{\circ}C$ and titrate with standard EDTA solution until the colour changes from red to orange yellow. The addition of the titration was made drop wise near the end point since the colour change was normally altogether sharp.

The strength of the Cobalt solution was calculated using the reaction.

1.0 ml., 0.1M, EDTA = 5.89 mg. Co^{+2}

[A] Synthesis of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt (II) complex: $[Co(C_{19}H_{10}O_4Cl_2)_2]$:

Cobalt chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-

chromen-2-one] [Chal-AX(0.1M)]on a water bath for half an hour when *dark purple blue*-precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 300^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was determined by the method as described in Chapter–2 on page 65. The result is presented in Table – II on page 110.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was determined by Rast's camphor method. The method is described in Chapter – 2 on page 66. The result is presented in the Table – II on page 110.

Elemental Analysis:

This involved the estimation of cobalt, carbon and hydrogen present in the bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex were determined using the method as described in Chapter–2 on page 67. The result is presented in the Table – II on page 110.

Absorption Spectra of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex

Absorption Spectra of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was taken using Backmann spectrophotometer. The optical density at different wavelength was recorded. The result are summarized in Table–I on page 109. The nature of absorption curve is shown in fig6A on page 123.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was measured by Gouy balance method. The method is described in Chapter – 2 on page 71. The result is presented III on page 111.

[B] Synthesis of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt (II) complex : $[Co(C_{19}H_{10}O_4Cl_2)_2]$:

Cobalt chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-BX (0.1M)] on a water bath for half an hour when a *dark red* precipitates of cobalt complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100°C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complexes do not show clear melting point. It gets char at temperature above $280^{o}C$.

Conductivity Measurement:

The conductivity of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was determined by the method as described in Chapter-2 on page 65. The result is presented in Table-II on page 110.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 110.

Elemental Analysis:

Estimation of cobalt, carbon and hydrogen present in the bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 110.

Absorption Spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] Cobalt(II) complex :

Absorption spectra of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was taken using Backmann spectrophotometer. Their optical density at different wavelengths was recorded.

The results of absorption curves are shown in table-I on page 109. The nature of absorption curve is shown in fig6B on page 124.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] cobalt(II) complex was measured by Gouy-balance Method. The method is descried on page 71. The result is presented in Table-III on page 111.

[D] Synthesis of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Cobalt (II) complex :[$Co(C_{19}H_{11}O_4Cl)_2$] :

Cobalt chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex [Chal-DY(20 ml, 0.1M)]on a water bath for half an hour when *dark brown* precipitates of cobalt complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conducitivity of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was determined by the method as described in chapter-2 on page 65. The result is presented in Table-II on page 110.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 110.

Elemental Analysis:

Estimation of cobalt, carbon and hydrogen present in the bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-6-methyl-2H-chromen-2-one] cobalt(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 110.

Absorption Spectra of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex

Absorption spectra of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 109. The nature of absorption curve is shown in fig6D on page 125.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was measured by Guoy-balance Method. The method is descried in Chapter-2 on page 71. The result is presented in Table-III on page 111.

[E] Synthesis of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt (II) complex : $[Co(C_{19}H_{11}O_4Cl)_2]$:

Cobalt chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml. of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] [Chal-EY (20 ml, 0.1M)]on a water bath for half an hour when *dark green* precipitates of nickel complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 110.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 100.

Elemental Analysis:

Estimation of cobalt, carbon and hydrogen present in the bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex were determined using the method as described in chapter-2 on page 67. The result as described in Table-II on page 110.

Absorption Spectra of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex :

Absorption spectra of [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 109. The nature of absorption curve is shown in fig6E on page 126.

Magnetic Susceptibility:

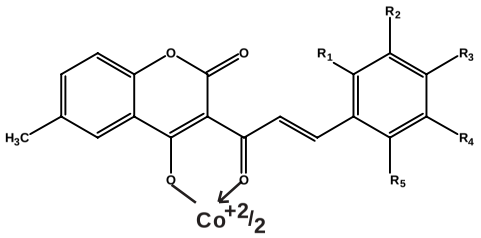
Magnetic Susceptibility of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] cobalt(II) complex was measured by Gouy-balance Method. The method is described in Chapter-2 on page 71. The result is presented in Table-III on page 111.

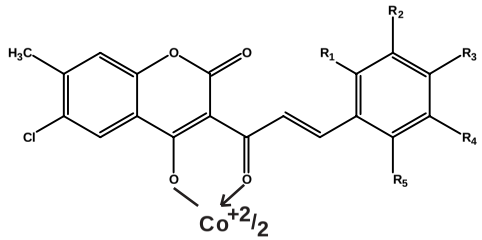
TABLE-I

Absorption maximum (λ max) and log ε of metal complexes.

SR. NO.	METAL COMPLEXES	λ max. (nm)	log ε
1	Co (Chal-AX)$_2$	394.60	2.970
		365.10	2.991
		318.30	3.187
		291.30	3.005
		469.30	0.050
2	Co (Chal-BX)$_2$	350.00	3.003
		301.20	3.291
		281.50	3.302
		488.00	0.040
3	Co (Chal-DY)$_2$	322.80	1.155
		282.50	1.207
		259.30	1.228
		540.60	0.032
		466.40	0.047
4	Co (Chal-EY)$_2$	347.60	2.293
		340.40	2.288
		328.40	2.313
		285.10	2.336
		635.80	0.418

TABLE-II
ANALYTICAL DATA OF METAL CHELATES





Where R_1, R_2 and R_3 are described on page 33, 34

Sr. No.	NAME OF METAL CHELATES	MOLECULAR FORMULA	MOLECULAR WEIGHT	% OF CARBON		% OF HYDROGEN		% OF COBALT		CONDUCTIVITY Mohs cm^2
				CAL	FOUND	CAL	FOUND	CAL	FOUND	
1	Co(Chal AX)$_2$	Co($C_{19}H_{12}O_4Cl_2$)$_2$	804.93	51.34	51.31	1.42	1.38	10.50	10.57	9.6
2	Co(Chal BX)$_2$	Co($C_{19}H_{12}O_4Cl_2$)$_2$	804.93	52.10	52.07	1.55	1.53	9.14	9.10	9.2
3	Co(Chal DY)$_2$	Co($C_{19}H_{13}O_4Cl$)$_2$	736.93	50.95	50.91	1.23	1.19	6.58	6.55	10.5
4	Co(Chal EY)$_2$	Co($C_{19}H_{13}O_4Cl$)$_2$	736.93	56.65	56.62	1.36	1.33	7.32	7.28	10.1

TABLE-III
MAGNETIC SUSCEPTIBILITY OF METAL CHELATES

* **Current : 6 Amps.**
* **α = 0.0384 x 10^{-6} C.G.S.**
* **β = 0.3008 x 10^{-6} C.G.S.**
* **Temp. = 300^0 K**

Sr.	Molecular Formula	Molecular Weight	Amount of Compound in g. (m)	Force of magnetic field 'F' in g.	$\chi = \beta F + \alpha / m$	$\chi M = \chi.M.$ 10^{-6} C.G.S.	$\chi M^{Corr} = \chi.M - M^{Corr}$ 10^{-6}C.G.S.	μeff B.M.	N un ele
1	$Co(C_{19}H_{12}O_4Cl_2)_2$	804.93	0.3548	2.4011	2.1438	1202.57	1481.97	1.89	
2	$Co(C_{19}H_{12}O_4Cl_2)_2$	804.93	0.3738	2.4328	2.0604	1328.81	1638.87	1.99	
3	$Co(C_{19}H_{13}O_4Cl)_2$	736.93	0.4802	2.3552	1.5552	1391.86	1885.80	2.13	
4	$Co(C_{19}H_{13}O_4Cl)_2$	736.93	0.4589	2.3761	1.6411	1321.02	1754.76	2.06	

CHAPTER - 5

SYNTHESIS AND ANALYTICAL STUDY OF IRON COMPLEXES

CHAPTER – 5

SYNTHESIS AND ANALYTICAL STUDY OF IRON COMPLEXES:

Experimental

PREPARATION OF STANDARD SOLUTIONS:

Ferrous ammonium sulphate [$FeSO_4(NH_4)_2SO_4.6H_2O$):

Ferrous ammonium sulphate (A.R., B.D.H. 39.214g., 0.1M) was dissolved in distilled water, acidified with hydrochloric acid (A.R.) and made to 1 lit. to get a decimolar solution. It was standardized with 0.1M $KMnO_4$ solution.

Procedure:

Pipette 25ml. of ferrous ammonium sulphate solution, add few ml. of syrupy phosphoric acid and titrate with potassium paramagnet solution till slight pink colour is obtained.

The strength of the ferrous ammonium sulphate solution was calculated using the relation.

1.0 ml., 0.1M, $KMnO_4$ = 5.58 mg. Fe^{+2}

[A] Synthesis of bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex : $[Fe(C_{19}H_{10}O_4Cl_2)_2]$:

Ferrous ammonium sulphate solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 5.0-6.0. It was refluxed with excess of alcoholic solution of [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-AX(0.1M)]on a water bath for half an hour when *dark purple blue*-precipitates of iron complex were obtained. The

precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron (II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 300^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron (II) complex was determined by the method as described in Chapter–2 on page 65. The result is presented in Table – II on page 121.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was determined by Rast's camphor method. The method is described in Chapter – 2 on page 66. The result is presented in the Table – II on page 121.

Elemental Analysis:

This involved the estimation of iron, carbon and hydrogen present in the bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex were determined using the method as described in Chapter–2 on page 67. the result is presented in the Table – II on page 121.

Absorption Spectra of [3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex

Absorption Spectra of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was taken using Backmann spectrophotometer. The optical density at different wavelength was recorded. The result are summarized in Table–I on page 120. The nature of absorption curve is shown in fig6A on page 123.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was measured by Gouy balance method. The method is described in Chapter – 2 on page71. The result is presented III on page 122.

[B] Synthesis of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron (II) complex : [$Fe(C_{19}H_{10}O_4Cl_2)_2$]:

Iron chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml of water) was added to get the pH between 5.0-6.0 It was refluxed with excess of alcoholic solution of [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] [Chal-BX(20ml, 0.1M)] on a water bath for half an hour of iron complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complexes do not show clear melting point. It gets char at temperature above $280^{o}C$.

Conductivity Measurement:

The conductivity of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was determined by the method as described in Chapter-2 on page 65. The result is presented in Table-II on page 121.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 121.

Elemental Analysis:

Estimation of iron, carbon and hydrogen present in the bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 121.

Absorption Spectra of bis [3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex :

Absorption spectra of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was taken using Backmann spectrophotometer. Their optical density at different wavelengths was recorded.

The results of absorption curves are shown in table-I on page 120. The nature of absorption curve is shown in fig6B on page 124.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] iron(II) complex was measured by Gouy-balance Method. The method is descried on page 71. The result is presented in Table-III on page 122.

[D] Synthesis of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Iron (II) complex : [Fe($C_{19}H_{11}O_4Cl)_2$] :

Iron chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (30g. in 10ml. of water) was a added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex [Chal-DY(20 ml, 0.1M)]on a water bath for half an hour when *light coffee* precipitates of iron complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was determined by the method as described in chapter-2 on page 65. The result is presented in Table-II on page 121.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 121.

Elemental Analysis:

Estimation of iron, carbon and hydrogen present in the bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Nickel(II) complex were determined using the method as described on page 67. The result as described in Table-II on page 121.

Absorption Spectra of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Iron(II) complex

Absorption spectra of bis [3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 120. The nature of absorption curve is shown in fig 6D on page 125.

Magnetic Susceptibility:

Magnetic Susceptibility of bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Iron(II) complex was measured by Gouy-balance Method. The method is descried in Chapter-2 on page 71. The result is presented in Table-III on page 122.

[E] Synthesis of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Iron (II) complex :[Fe($C_{19}H_{11}O_4Cl)_2$] :

Iron chloride solution (10.0ml., 0.1M) diluted to 50 ml. and excess of ammonium hydroxide and ammonium acetate (3.0g in 10ml. of water) was added to get the pH between 10.5-11.0 It was refluxed with excess of alcoholic solution of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] [Chal-EY (0.1M)]on a water bath for half an hour when *dark coffee* precipitates of iron complex were obtained. The precipitates were filtered, washed with distilled water and dried at 100^{o}C. The complex was crystallized from DMF.

Solubility:

Bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex is insoluble in water, slightly soluble in methanol, ether, chloroform, benzene and other organic solvents. It is soluble in DMF, DMSO.

The complex do not show clear melting point. It gets char at temperature above 280^{o}C.

Conductivity Measurement:

The conductivity of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was determined by the method as described on page 65. The result is presented in Table-II on page 121.

Molecular Weight Determination:

The molecular weight of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was determined by Rast's camphor method. The method is described in Chapter-2 on page 66. The result is presented in Table-II on page 121.

Elemental Analysis:

Estimation of iron, carbon and hydrogen present in the bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex were determined using the method as described in chapter-2 on page 67. The result as described in Table-II on page 121.

Absorption Spectra of bis [3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] Iron(II) complex :

Absorption spectra of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was taken using Backmann Spectrophotometer. The optical density at different wavelengths were recorded. The results of absorption curves are shown in table-I on page 120. The nature of absorption curve is shown in fig6E on page 126.

Magnetic Susceptibility:

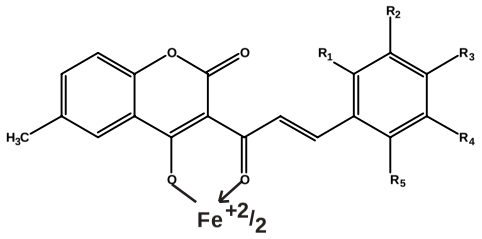
Magnetic Susceptibility of bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] iron(II) complex was measured by Gouy-balance Method. The method is described in Chapter-2 on page 71. The result is presented in Table-III on page 122.

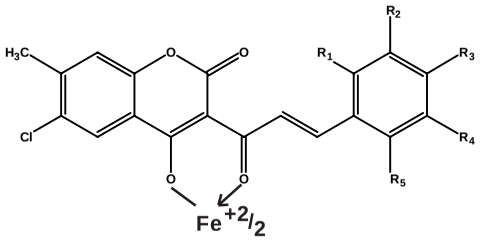
TABLE-I

Absorption maximum (λ max) and log ε of metal complexes.

SR. NO.	METAL COMPLEXES	λ max. (nm)	log ε
1	Fe (Chal-AX)$_2$	341.20	3.215
		322.00	3.712
		301.40	3.805
		285.50	3.698
		680.50	0.416
2	Fe (Chal-BX)$_2$	374.00	3.009
		291.60	3.498
		277.80	3.511
		589.90	0.029
3	Fe (Chal-DY)$_2$	334.70	1.665
		297.50	1.673
		282.00	1.605
		602.50	0.087
4	Fe (Chal-EY)$_2$	340.60	2.695
		334.20	2.507
		302.00	2.416
		509.20	0.052

TABLE-II
ANALYTICAL DATA OF METAL CHELATES





Where R_1, R_2 and R_3 are described on page 33, 34

Sr. No.	NAME OF METAL CHELATES	MOLECULAR FORMULA	MOLECULAR WEIGHT	% OF CARBON		% OF HYDROGEN		% OF COBALT		CONDUCTI Mohs cı
				CAL	FOUND	CAL	FOUND	CAL	FOUND	
1	Fe(Chal AX)$_2$	Fe($C_{19}H_{12}O_4Cl_2$)$_2$(H_2O)$_2$	837.85	48.50	48.47	3.36	3.33	9.40	9.47	11.2
2	Fe(Chal BX)$_2$	Fe($C_{19}H_{12}O_4Cl_2$)$_2$(H_2O)$_2$	837.85	49.57	49.55	3.54	3.52	8.24	8.21	11.8
3	Fe(Chal DY)$_2$	Fe($C_{19}H_{13}O_4Cl$)$_2$(H_2O)$_2$	769.85	49.14	49.12	2.80	2.77	6.02	6.00	10.5
4	Fe(Chal EY)$_2$	Fe($C_{19}H_{13}O_4Cl$)$_2$(H_2O)$_2$	769.85	54.42	54.39	3.10	3.08	6.66	6.63	11.6

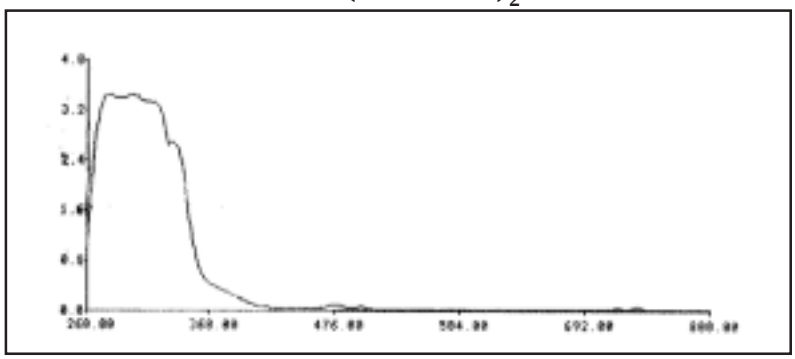
TABLE-III
MAGNETIC SUSCEPTIBILITY OF METAL CHELATES

* **Current : 6 Amps.**
* **α = 0.0384 x 10^{-6} C.G.S.**
* **β = 0.3008 x 10^{-6} C.G.S.**
* **Temp. = 300^0 K**

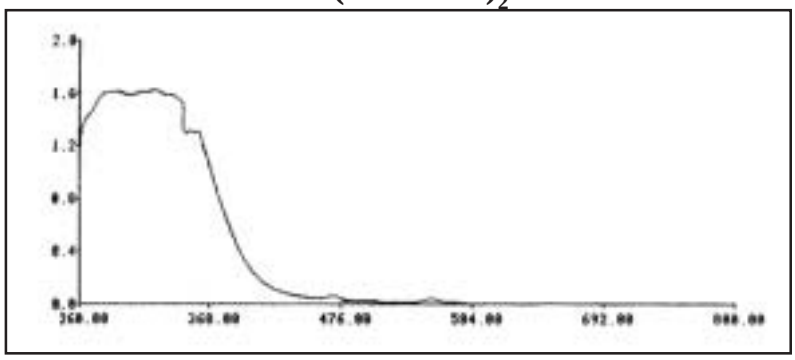
Sr.	Molecular Formula	Molecular Weight	Amount of Compound in g. (m)	Force of magnetic field 'F' in g.	$\chi = \beta F + \alpha / m$	$\chi M = \chi . M.$ 10^{-6} C.G.S.	$\chi M^{Corr} = \chi . M - M^{Corr}$ 10^{-6}C.G.S.	μeff B.M.	u e
1	$Fe(C_{19}H_{12}O_4Cl_2)_2(H_2O)_2$	837.85	0.3371	-2.4271	-2.2796	-1353.77	-1074.37	-	Dia
2	$Fe(C_{19}H_{12}O_4Cl_2)_2(H_2O)_2$	837.85	0.3562	-2.4586	-2.1840	-1480.43	-1170.37	-	Dia
3	$Fe(C_{19}H_{13}O_4Cl)_2(H_2O)_2$	769.85	0.4552	-2.3819	-1.6583	-1538.68	-1043.74	-	Dia
4	$Fe(C_{19}H_{13}O_4Cl)_2(H_2O)_2$	769.85	0.4107	-2.4015	-1.8523	-1552.01	-1118.27	-	Dia

Fig. - 6A
ABSORPTION SPECTRA OF THE COMPLEXES

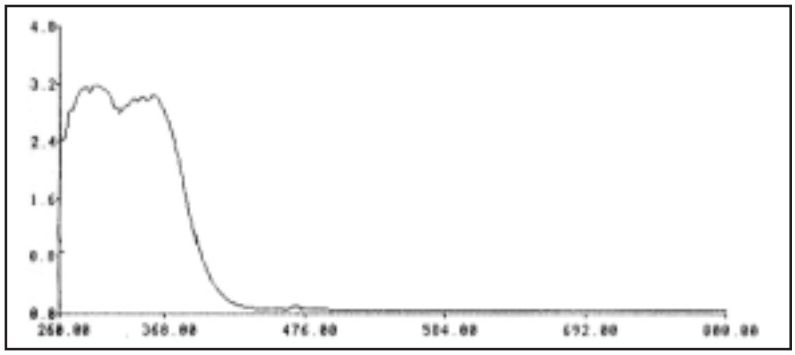
$Cu(Chal\ AX)_2$



$Ni(Chal\ AX)_2$



$Co(Chal\ AX)_2$



$Fe(Chal\ AX)_2$

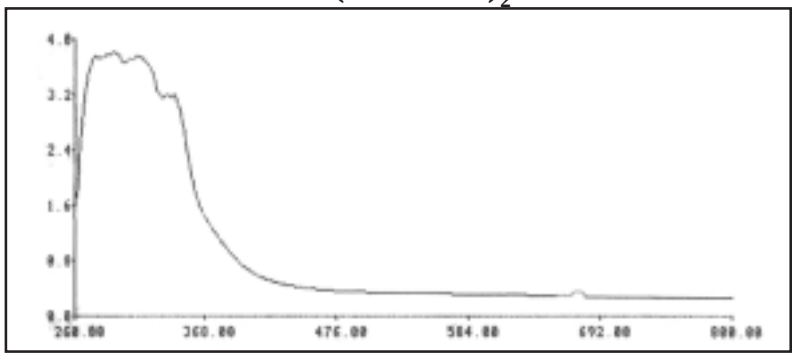
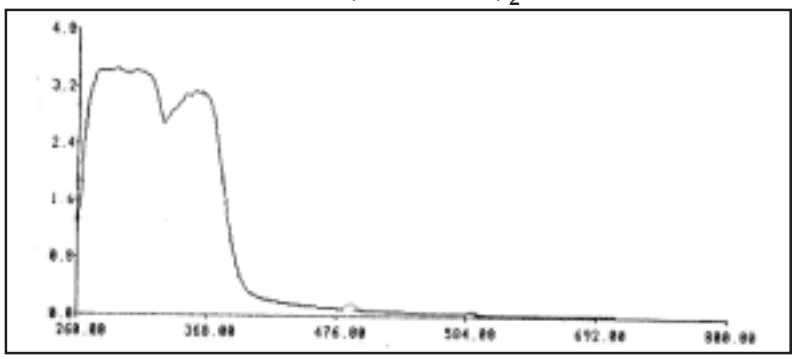
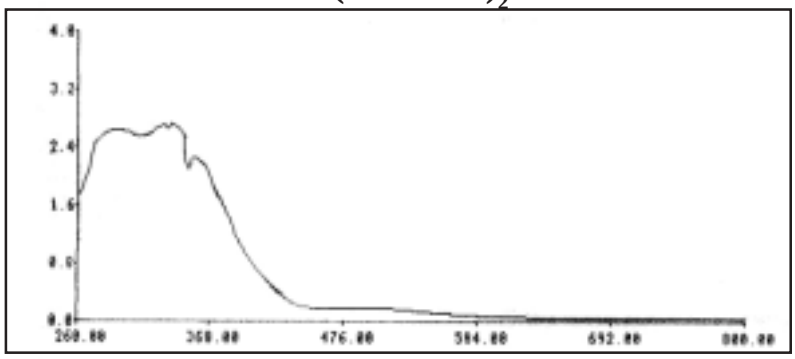


Fig. - 6B
ABSORPTION SPECTRA OF THE COMPLEXES

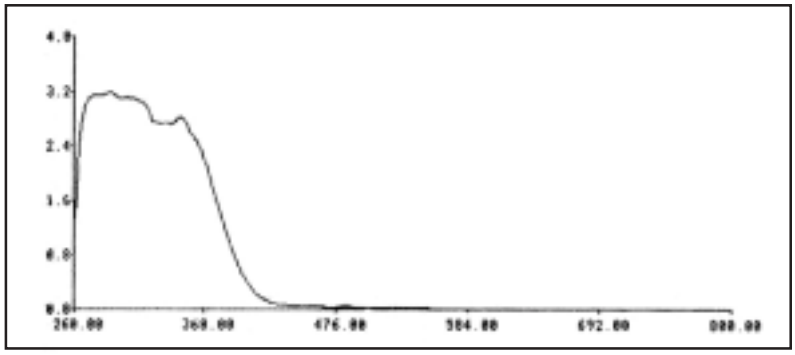
$Cu(Chal\ BX)_2$



$Ni(Chal\ BX)_2$



$Co(Chal\ BX)_2$



$Fe(Chal\ BX)_2$

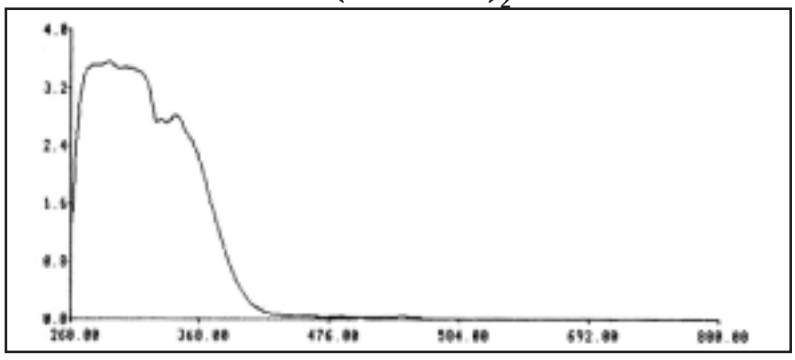
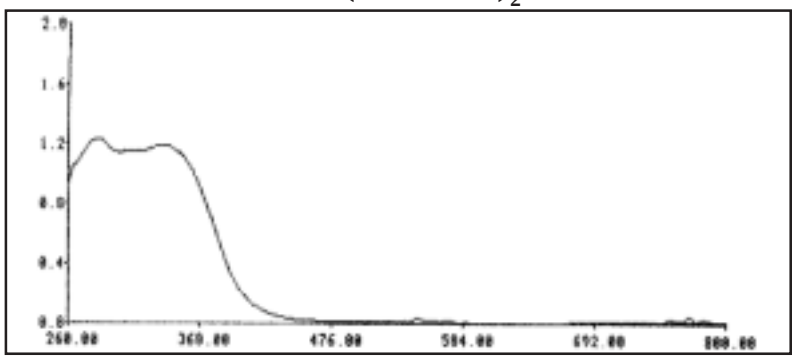
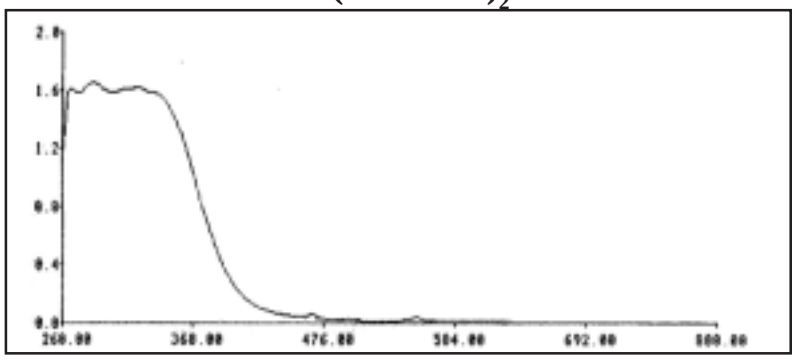


Fig. - 6D
ABSORPTION SPECTRA OF THE COMPLEXES

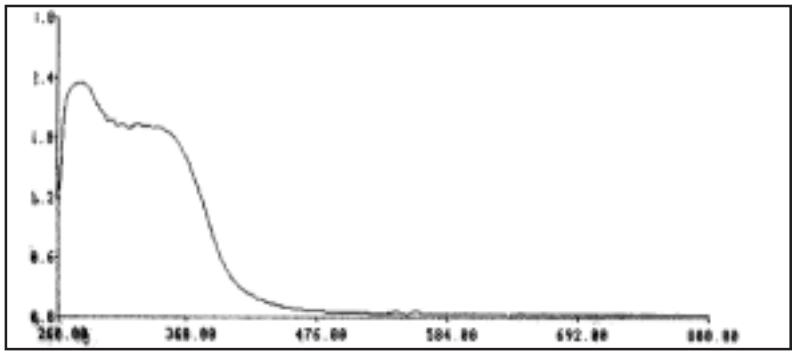
$Cu(Chal\ DY)_2$



$Ni(Chal\ DY)_2$



$Co(Chal\ DY)_2$



$Fe(Chal\ DY)_2$

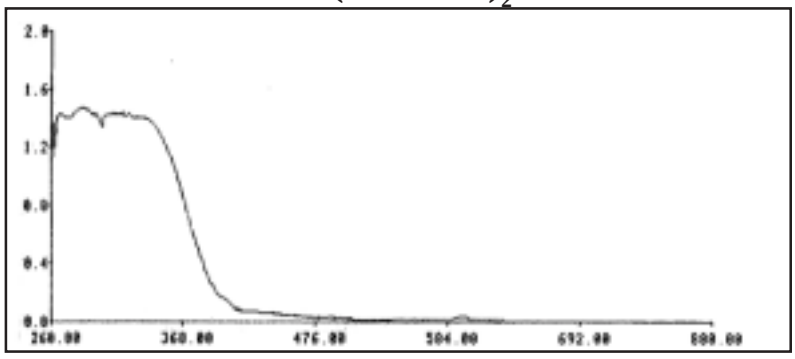
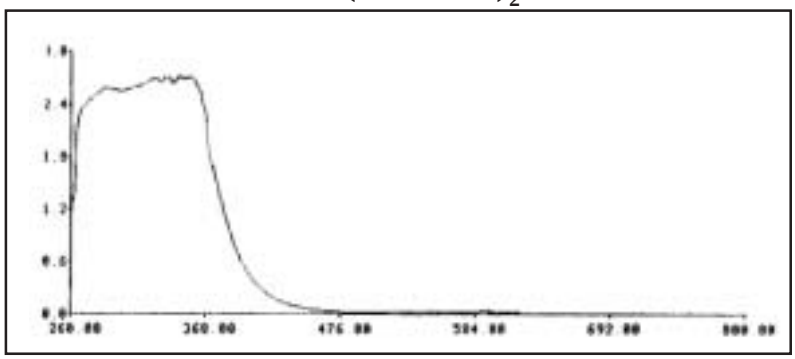
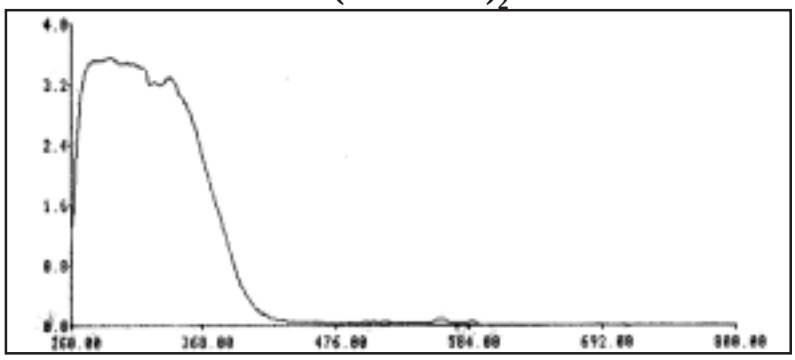


Fig. - 6E
ABSORPTION SPECTRA OF THE COMPLEXES

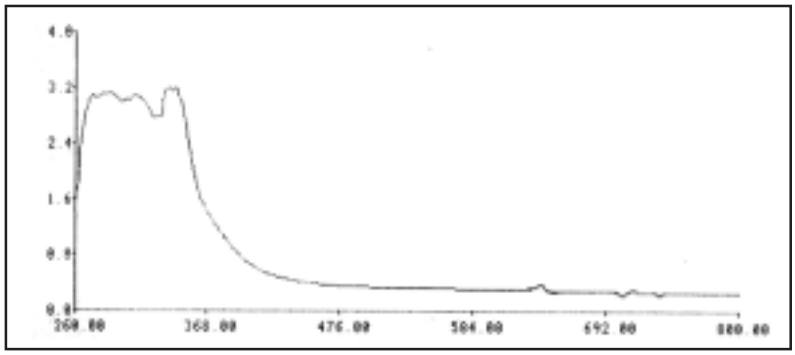
$Cu(Chal\ EY)_2$



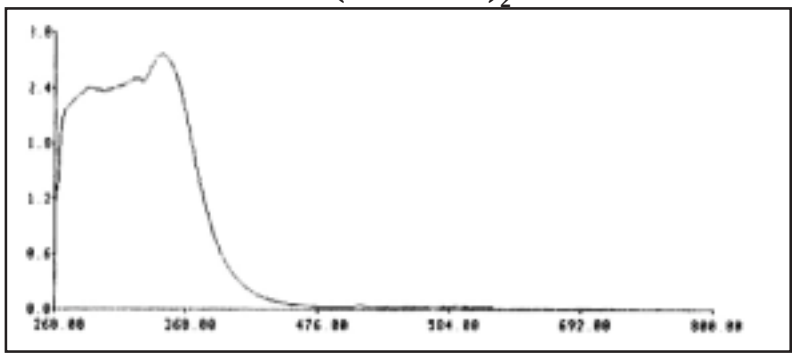
$Ni(Chal\ EY)_2$



$Co(Chal\ EY)_2$



$Fe(Chal\ EY)_2$



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PART - II

POTENTIOMETRIC DETERMINATION OF STEPWISE STABILITY CONSTANTS OF METAL COMPLEXES

THEORETICAL

The stepwise formation of metal chelate MLn can be represented in reversible equilibria already discussed in the general introduction.

$$M + L \rightleftharpoons ML$$

$$ML + L \rightleftharpoons ML_2$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad \text{---------(1)}$$

Where M is the uncomplexed central metal ion and L is a monodentate ligand. (Charge on M or L on a complex species formed are omitted). each step is governed by the corresponding equilibrium constant defined as -

$$^{T}K_n = \frac{[\,MLn\,]}{[MLn\text{-}1][L]} \qquad \text{---------(2)}$$

Where $^{T}K_n$ is the activity quotient for the reaction step.

$$ML_{n-1} + L \rightleftharpoons MLn \qquad \text{--------(3)}$$

It is called the n^{th} thermodynamic metal-ligand stability or formation constant. the overall reaction is represented as -

$$M + nL \rightleftharpoons MLn \qquad \text{---------(4)}$$

and the activity quotient for the overall equilibria is ...

$$^{T}\beta_n = \frac{[MLn]}{\{M\}\{L\}^n} \qquad \text{----------(5)}$$

The overall and stepwise stability constants are related as

$$^{T}\beta_n = {}^{T}K_1 . {}^{T}K_2 \ldots {}^{T}K_n = \prod_{n=1}^{n=n} T_{K_n} \qquad \text{----------(6)}$$

The ligand as be considered as a weak acid associated with ionizable proton. The stepwise formations of LHj. Ligands can also be represented by J equilibria as -

$$L + H \rightleftharpoons LH$$

$$LH + H \rightleftharpoons LH_2$$

$$LH_{J-1} + H \rightleftharpoons LH_J \qquad \text{---------(7)}$$

The equilibrium constant can be represented as -

$${}^{T}K_J\,H = \{LH_J\} / \{LH_{J-1}\}\,\{H\} \qquad \text{---------(8)}$$

Where, ${}^{T}K_JH$ is J^{th} thermodynamic proton-ligand stability constant. It reciprocal of the thermodynamic dissociation constant of the acid LH_J.

The overall thermodynamic proton-ligand stability constant is given by.....

$${}^{T}ß_JH = \{LH_J\} \Big/ \{L\}\,\{H\} \qquad \text{----------(9)}$$

The corresponding overall reaction equilibria is

$$L + JH \rightleftharpoons LH_J \qquad \text{---------(10)}$$

It is related to the successive stability constant as .....

$${}^{T}H_J = {}^{T}K_1H \;.\; {}^{T}K_2H \ldots {}^{T}K_JH = \prod_{J=1}^{J=J} {}^{T}K_JH \qquad \text{---------(11)}$$

It is assumed that ionic or molecular species involving M,L and H other than those shown in the above equilibria do not exist in solution. This is equivalent to assume that absence of polynuclear complexes, proton-bearing complexes, unionized metal salt and hydroxy-bearing complexes and metal ions.

The thermodynamic constants referred to above are difficult to determine, especially in systems in which the complexity is slight or in which several complexes co-exist. In such cases, the activity co-efficients are controlled by using an inert supporting elecrolyte and to determine stability constants will be valid in that particular salt medium. These constants are known as stoichiometric, or apparent

or concentration constants. The equilibrium constants can be represented using concentration terms i.e., in moles per litre.

$$\text{Thus, } K_n = [ML_n] / [ML_{n-1}] [L] \qquad \text{---------(12)}$$

Where K_n is known as n^{th} stoichiometric metal-ligand stability or formation constant.

$$\beta n = \frac{[MLn]}{[M][L]^n} \qquad \text{----------(13)}$$

where βn is the n^{th} overall stoichiometric metal-ligand stability constant.

Similarly, stoichiometric proton-ligand stability constants are given by.....

$$K_J^H = \frac{[LH_J]}{[LH_{J-1}][H]} \qquad \text{---------(14)}$$

$$\text{and} \quad ß^H_J = [LH_J] / [L][H]^J \qquad \text{---------(15)}$$

it is related to the successive stoichiometric proton-ligand stability constant as -

$$\beta_J^H = K_1^H . K_2^H . K_3^H .....K_J^H = \prod_{J=1}^{J=J} K_J^H$$

Rossotti and Rossotti[1] have discussed the choice of a suitable salt medium and have pointed out the limitations of the constant ionic medium. Sodium per chlorate is the most frequently used supporting electrolyte because of very slight complexing tendency of per chlorate ion. Generally, the competition between per chlorate ion and the ligand under study is of minor importance. It may be mentioned here that molar concentrations are used in place of activities throughout the subsequent treatment.

Determination of stability constants:

In order to determine the values of n formation constants. Bjerrum[2] introduced the concept of degree of formation of the system or the average ligand number n, which he defined as the average number of ligands bound per metal ion.

$$\text{i.e. } \bar{n} = \frac{1[ML]+2[ML_2]+....+n[MLn]}{[M]+[ML]+[ML_2]+....+[MLn]} = \frac{\sum_{n=1}^{n} n[MLn]}{\sum_{n=0}^{n} n[MLn]} \qquad \text{---------(16)}$$

Substituting for the value of MLn from equation of the type (12)and elimination [M], n is obtained in terms of free ligand concentration [L] and the formation constants K_1, K_2, ------ K_n.

$$\bar{n} = \frac{K_1[L]+2K_1K_2[L]^2+....+nK_1K_2...K_n[L]^n}{1+K_1[L]+K_1K_2[L_2]^2+....+K_1K_2...K_n[L]^n} \qquad \text{---------(17)}$$

$$\sum_{n=1}^{n} n\beta n[L]^n \Big/ \sum_{n=0}^{n} \beta n[L]^n; (\beta_0 = 1) \qquad \text{---------(18)}$$

Eq. (18) is the so called Bjerrum formation of the system[2]. For a mononuclear system $\bar{n}$, is a function only of a free ligand concentration [L].

A similar function for the proton ligand system is given by..

$$\bar{n}_A = \frac{K_1^H[H]+2K_1^H[H]K_2^H[H]^2+...+JK_1^HK_2^HK_3^H....K_J^H[H]^J}{1+K_1^H[H]+K_1^H[H]K_2^H[H]^2+...+K_1^HK_2^HK_3^H....K_J^H[H]^J} \qquad \text{----------(19)}$$

Where, $\bar{n}A$ is the average number of hydrogen ions bound to each ligand that is not complex-bound. Using eq. (15)

$$\bar{n}A = \frac{\sum_{J=1}^{J} J.\beta_J^H[H]^J}{\sum_{J=0}^{n} .\beta_J^H[H]^J} \left\{\beta_0^H = 1\right\} \qquad \text{----------(20)}$$

Now for a mononuclear system, such system, such as that one defined by equilibria described earlier.

$$T_M = \sum_{n=0}^{n} [ML]_n \qquad \text{----------(21)}$$

and $$T_L = \sum_{J=0}^{J} [LH_J] + \sum_{n=0}^{n} n[MLn] \qquad \text{----------(22)}$$

Where T_M and T_L are the total concentrations, in moles per liter of the central metal ion and the ligand present in the system. Using eq.(13) and equation (21) can be expressed as-

$$T_M = [M] + \sum_{n=0}^{n} \beta n[L]^n \qquad \text{----------(23)}$$

and using (13) and (14) equation (22) becomes

$$T_L = [L] + \sum_{J=0}^{J} \beta_J^H [H]^J + M \sum_{n=0}^{n} \beta n[L]^n \qquad \text{----------(24)}$$

Hearon and Gilbert[3] have pointed out that the expression for the free ligand concentration can be derived alternatively in terms of Electro neutrality relationship.

$$\sum_{I=0}^{I} Z_1 [I] + \sum_{J=0}^{J} (j - Z_L)[LHj] + \sum_{n=0}^{n} (Z_M - nZ_L)[MLn] = 0 \qquad \text{----------(25)}$$

The terms Z_I, Z_M and Z_L are the valences of the species I, M and L; I denote any species, such as H, OH or medium ions that contains neither M nor L. From equation (21), (22) and (23) it follows that...

$$\sum_{J=0}^{J} J[LH_J] = Z_L \cdot T_L - Z_M \cdot T_M - \sum_{I=0}^{I} Z_I \cdot [I] \qquad \text{----------(26)}$$

and $$a = \frac{Z_L \cdot T_L - Z_M \cdot T_M - \sum_{I=0}^{I} Z_I \cdot [I]}{\sum_{J=0}^{J} j\beta_J^H h^J} \qquad \text{----------(27)}$$

Where h is the free hydrogen ion concentration a, is the free ligand concentration. Thus 'a' can be obtained from equation (27), provided the values of h and $ß_J^H$ are known, since T_L and T_M, are known from the stoichiometry of the solution. The corresponding value of $\bar{n}$ can then be obtained from....

$$\bar{n} = \frac{T_L - a \sum_{J=0}^{J} \beta_J^H h^j}{T_M} \qquad \text{————————-(28)}$$

This method of competitive complex formation was introduced by Bjerrum[2] and had been very widely used to study systems in which the ligand was the conjugate base of a weak acid. Since 'h' was usually determined potentiometrically the quantity measured was linear function of log h and hydrogen ion concentrations in the range $1M > h > 10^{-14}$ can be determined, provided that the appropriate electrodes were available.

The plot of $\bar{n}$ versus reciprocal of free ligand concentrations 1/L or versus ligand exponent, pL (log 1/L) is known as formation curve of the metal ligand system.

The determination of stability constants from experimental data comprises the following three steps. In the present case third step has not been done.

1. Evaluation of the formation curve of the system.
2. Calculation of stochiometric K_n of the system by directs solution of the formation function.
3. Conversion of stochiometric constants into thermodynamic constants.

Evaluation of the formation curve:

Bjerrum - Calvin pH titration technique is widely used for the evaluation of the formation curve. Here [H] is measured potentiometrically using different pH electrodes, predominantly glass electrodes, and the titration technique allows a large amount of data to be obtained in a short period of time. The method as adopted by Irving and Rossotti[4] has several advantages. Here it is neither necessary to convert

the pH meter reading to stoichiometric hydrogen ion concentration nor to know the stoichimetric concentration of the neutral salt added to maintain constant ionic strength. The method is valid both in water and water-dioxane mixture which are often required to be used to provided homogeneous systems. Moreover, the acid dissociation constants of the chelating agents, which are essential in the calculations, are obtained under the same experimental conditions as the metal ligand formation constants. Because of such an advantage this method is employed in the present work.

The method of lrving and Rossotti[4]:-

Before starting pH measurements of each set, the pH meter scale was calibrated using two standard aqueous buffer solutions. A 0.05-M potassium hydrogen phthalate solution was used as the fixed standard and its accuracy in the alkaline range was checked with 0.1 M borax solution. The exact pH values of these buffers recorded from the literature are given below:

Temperature ^{0}C	**M/20 potassium Hydrogen phthalate**	**M Borax**
15	3.98	9.26
25	4.00	9.17
35	4.01	9.08
40	4.03	9.05
45	4.04	9.03

The pH meter reading 'B' plotted against volume of alkali used to titrate:

1. A mixture containing a mineral acid, a metal salt, a chelating agent and a neutral electrolyte to keep ionic strength constant.
2. A mixture same as (1) above but without the metal salt.
3. A mixture same as (1) above but without metal salt and the chelating agent.

In all these three mixture, the ionic strength, initial total volume and temperature were kept constant. The titration was carried under an inert atmosphere of nitrogen against standard alkali solution.

The titration curves obtained by plotting 'B' against volume of alkali added were designated as the metal titration curve, the ligand titration curve and the acid titration curve respectively. From the displacement of the ligand curve, $\bar{n}_A$ was calculated and from the displacement of the metal-curve from the ligand curve $\bar{n}$ was calculated.

The use of a pH meter, calibrated with an aqueous buffer is restricted of course, to aqueous solutions. However, when the mixed aqueous media, especially aqueous dioxane solution or other are employed to keep the metal chelate in a homogeneous medium, the true value of pH corresponding to aqueous solution can be calculated from the pH meter reading B by-using Van Uitert and Hass[5] relation.

$$- \log [H] = B + \log f + \log U_H^0 \qquad \text{--------(29)}$$

Where f is the activity coefficient of the hydrogen ions in the solvent mixture under consideration at the same temperature and ionic strength and U_H^0 is a correction factor at zero ionic strength, which depends only on the solvent composition and temperature. U_H^0 is equal to unity in aqueous media. The value of f can be obtained by interpolation from the tables of Harned and Owen[6] and the of U_H^0 from fig. 2 of Van Uiterr and Hass's[5] paper. The meter reading B in any aqueous dioxane solution can, therefore, be translated into hydrogen ion concentration using eq.(29) provided the correction factor has been determined for the appropriate solvent, salt medium and temperature.

eq. (29) can be written as

$$\frac{1}{\text{antilog } B} = [H] \,.\, f \,.\, U_H^0 \qquad \text{-------(30)}$$

$$[H] = \frac{1}{f \,.\, U_H^0} \,.\, \frac{1}{\text{antilog } B} \qquad \text{-------(31)}$$

Substituting for [H] in eq. (19) we have

$$\bar{n}_A = \frac{K_1^H \cdot \frac{1}{F U_H^0} \cdot \frac{1}{\text{antilog ß}} \pm \frac{2K_1^H K_2^H}{(f \cdot U_H^0)2} \cdot \frac{1}{(\text{antilog}\beta)^2} + \ldots\ldots +}{1 + \frac{K_1^H}{f U_H^0} \cdot \frac{1}{\text{antilog}ß} + \frac{K_1^H K_2^H}{(f \cdot U_H^0)^2} \cdot \frac{1}{(\text{antilog}\beta)^2} + \ldots\ldots +}$$

$$\frac{\frac{JK_1^H K_2^H \ldots\ldots K_J^H}{(f.U_H^{\,0})^J} \cdot \frac{1}{(\text{antilog}\beta)^2}}{\frac{K_1^H K_2^H \ldots\ldots K_J^H}{(f.U_H^0)^J} \cdot \frac{1}{(\text{antilog}ß)^J}} \qquad \text{-------(32)}$$

Irving and Rossotti[4] define practical proton ligand stability constants, ${}^{P}K_J H$ as.....

$$K_J^H = f U_H^0 \cdot {}^{P}K_J{}^H \qquad \text{-------(33)}$$

and also $$\beta_J^H = (f U_H^0)^J \cdot {}^{P}\beta_J{}^H \qquad \text{-------(34)}$$

These can be obtained by the solution of (32) using methods described later. Hence $\bar{n}_A$ can be obtained in terms of proton ligand stability constants.

Calculation of $\bar{n}_A$, $\bar{n}$ and P_L:

From the titration curves (acid titration curve, ligand titration curve and metal titration curve), the average no. of proton associated with the ligand ($\bar{n}_A$); average no. of ligands attached per metal ion ($\bar{n}$) and free ligand exponent (pL) were calculate using the formulas of Irving and Rossotti[4].

$$\bar{n}_A = Y - \frac{(V'' - V')(N^0 + E^0)}{(V^0 + V')T_L^{\,0}} \qquad \text{--------(35)}$$

$$\bar{n} = \frac{(V''' - V'')(N^0 + E^0)}{(V^0 + V'')\,\bar{n}_A \,.\, T_M^0} \qquad \text{--------(36)}$$

$$P_L = \log_{10} \frac{\sum_{n=0}^{n} \beta_n^H \cdot \frac{1}{(\text{antilog}B)^n}}{T_L^0 - \bar{n}.T_M^0} \; x \frac{V^o + V'''}{V^o} \qquad \text{--------(37)}$$

Where V' , V'' and V''' are the volumes of alkali required to reach the same pH in the acid, ligand and metal titration curves respectitively. V_0 , T_L^0 and T_M^0 are the initial values of the mixtures, initial concentration of the ligand and initial concentrtation of metal ions; N^0 and E^0 are the concentration of the base and initial concentration of the acid and in the mixture, Y is the number of dissociable protons; and β_n^H is the overall proton ligand stability constant; 'B' is the pH meter reading.

Determination of stochiometric stbility constants:

A fairly large number of method for computing stability constants from experimental data have been used by number of authors[1,7,8] some of the more generally applicable computational method are as follows:

1. Method of solving simulatianeous equations derived from Bjerrum's formation function[2]

$$\sum_{n=0}^{n} (\bar{n} - n)\,[L]^n \,.\, \beta n = 0 \qquad \text{-------(38)}$$

2. Successive approximation method.[9]

from eq. (17) the following transformations were obtained

$$K_1 = \frac{1}{[L]} \cdot \frac{\bar{n}}{(1-\bar{n}) + (2-\bar{n})K_2[L]}$$

$$K_2 = \frac{1}{[L]} \cdot \frac{\bar{n} + (\bar{n}-1)K_1[L]}{(2-\bar{n})K_1[L]} \qquad \text{--------(39)}$$

Bjerrum[2] applied these equations to define the approximate constant obtained by other methods.

3. Interpolation at half $\bar{n}$ values.[9]

From N=2, the following relations may be derived from eq. (17):

$$\log K_1 = pL_{1/2} + \log [2/(1+\sqrt{1+12K_1/K_2}\,](n=1/2) \quad \text{--------- (40)}$$

$$\log K_2 = pL_{3/2} - \log [2/(1+\sqrt{1+12K_2/K_1}\,] \ (n=3/2) \quad \text{--------- (41)}$$

Where pL_a represents the free ligand exponent and a = $\bar{n}$; provided that $K_{n-1} >> K_n$. Approximately equal amounts of ML_{n-1}, and ML_n will be present in the solution when n = n - ½ and the contribution of ML_{n-2} , and ML_{n+1} may be neglected. We may write $\log K_n = pL_{n-1/2}$

Thus,

$$\log K_1 = pL_{1/2} \quad \text{--------- (42)}$$

$$\log K_2 = pL_{3/2} \quad \text{--------- (43)}$$

Unless $K_1/K_2 > 10^{2.5}$. this very commonly used approximation can introduces considerable error and in the case when N = 2, it has the disadvantage of using only two points on the formation curve. Kabadi et al.[10] have conclude the maximum permissible values of $\text{Log}(K_1/K_2)$ for certain desired accuracies half integral log K^1 value.

4. Interpolation at various $\bar{n}$ value[9]

The log K_1 and log K_2 are given by the equations.

$$\log K_1 = pL_{1-d} + \log \frac{1-d}{d} \quad \text{when } K_1 >> K_2 \quad \text{-------- (44)}$$

$$\log K_2 = pL_{1+d} - \log \frac{1-d}{d}$$

The use of these equation over the whole range of the formation curve (o<d<1) is only justified of $K_1 / K_2 > 10^4$ - If $K_1/K_2 < 10^4$ the calculated value of stability constant show a different, which was more pronounced for the lower valued of d.

5. Mid point slope method[9]

At the mid point of the formation curve where,

$\bar{n}$ =1 (system N = 2) $K_1K_2[L]^2 = 1$ or $\log K_1K_2 = 2pL_1$ --------- (45)

The abscises of the mid point will therefore give the value of the overall stability constant βn where precision is limited only by that of experimental measurements. The common practice of evaluating individual values K_1 and K_2 from the product K_1K_2 and eq. K_n - $pL_{n-1/2}$ demads a full appreciation of the implicate approximations and does not make full use of the experimental data. Bjerrum[2] defines spreading factor $x = \sqrt{K_1/4K_2}$ and relates to the mid point slope. D of the formation curve.

At $\bar{n}$ = 1, $D = -2.303/1+x$ --------- (46)

From the measured mid-point slope, D, the ratio K_1 / K_2, may be calculate and individual values of K_1 and K_2 were obtained by using K_1/K_2 values and relation $K_1K_2 = 2pL_1$. For N = 2, D, is given by…

$$D = \frac{-4.606}{2+\sqrt{K_1/K_2}}$$

and thus to introduce the concept of spreading factor was not necessary.

This method was only applicable where K_1 / K_2 lies between 10^3 and 10^{-2} (as $K_1/K_2 \rightarrow O, D \rightarrow -2.303$), and it uses only a very small portion of the formation curve in the region of the mid point. Significant errors may be introduced both in plotting the best formation curve to pass through the experimental points and in measuring its mid-point slope.

6. Schwarbenbach's Graphical method.[11]

The stability constants were obtained from experimental values of $\bar{n}$ and [L] by plotting values of $A = (\bar{n} - 1)[L] / \bar{n}$ and $B = (\bar{n} - 1) / (2 - \bar{n})$ [L] as abscissa and ordinates respectively. All lines passing through pairs of points (A,B) should intersect when exptrapolated at the point $(1/K_1K_2)$. This procedure is unreliable as lengthy extrapolation is necessary and is only suitable to experimental data of high precision.

7. Linear plots method.[1]

eq. (17) for N = 2 system may be written in form

$$yP_1 + xP_2 = 1 \qquad \text{-------- (47)}$$

Where x and y are functions of $\bar{n}$ and [L] and the parameters P_1 and P_2 are related to the stability constants. The six possible transformations of eq. (17) are -

$$\frac{1-\bar{n}}{\bar{n}}[L].\beta_1 + \frac{2-\bar{n}}{\bar{n}}.[L]^2.\beta_2 = 1 \qquad \text{-------- (48)}$$

$$\frac{\bar{n}}{(1-\bar{n})[L]}\frac{1}{} + \frac{1}{\beta_2}\frac{(\bar{n}-2)}{1-\bar{n}}[L]\Big/\beta_1 = 1 \qquad \text{-------- (49)}$$

$$\frac{\bar{n}}{(2-\bar{n})[L]^2}.\frac{1}{\beta_2} + \frac{\bar{n}\text{-}1}{(2-\bar{n})[L]}\beta_1\Big/\beta_2 = 1 \qquad \text{-------- (50)}$$

The other three transformations are obtained nearly be interchanging the values of x and y in the above equations. eq. (47) can be rearranged as -

$$Y = -\frac{P_2}{P_1}x + \frac{1}{P_1} \qquad \text{-------- (51)}$$

Thus if Y is plotted against x, a straight line of slope $-P_2/P_1$ and intercept $1/P_1$ should result. Such plots had been used by several authors.[12,13] They were quite convenient in cases were the measurements spread over a rather narrow range of free ligand concentration.

8. The correction term method [9]

eq. (50) for N = 2 can be written for the point (pL_{1-d}, 1-d) as

$$\log K_1 = {}^{P}L_{1-d} + \log\frac{2(1\text{-}d)}{d + \sqrt{d^2 + 4(1-d)^2.K_2\Big/K_1}} \qquad \text{---------- (52)}$$

Similarly, for the point (pL_{1+d}, 1+d),

$$\log K_2 = {}^{P}L_{1+d} + \log\frac{2(1\text{-}d)}{d + \sqrt{d^2 + 4(1-d)^2.K_2\Big/K_1}} \qquad \text{---------- (53)}$$

If the points are symmetrically disposed about the mid point ($\bar{n} = 1$) then,

$$pL_d = pL_{1-d} - pL_{1+d} = \log K_1 / K_2 - 2C \quad \text{---------- (54)}$$

Where the correction term C is given by

$$C = \frac{2(1-d)}{d + \sqrt{d^2 + 4(1-d)^2 . K_2/K_1}} \quad \text{---------- (55)}$$

For given value of K_1/K_2 and d,c was calculated and so pL_d and these were tabulated as well as graphically represented . The value of C corresponding to the measured value pL could be obtained from these graphs of tables.

C may be also be calculated from

$$C = \log\frac{1-d}{d} + \log\left\{1 - \frac{(1+d)[L]_{1-d}}{(1-d)[L]_{1+d}}\right\} \quad \text{---------- (56)}$$

If $K_1/K_2 > 10^4$ then C = log 1 - d/d and so C depends only on the value of d, therefore, log K_1 and log K_2 can be given by relations…….

$$\log K_1 = pL_{1-d} + \log\frac{1-d}{d} \quad \text{---------- (57)}$$

and

$$\log K_2 = pL_{1+d} - \log\frac{1-d}{d} \quad \text{---------- (58)}$$

Hence K_1 and K_2 were then calculated using eq. (57) and eq. (58). Similar calculations were made at several values of d and averages values of K_1 and K_2 were computed.

The correction term method is very rapid and reliable and makes use of many more experimental data, then Bjerrum's spreading factor method. However, it involves some *"smoothening"* of the experimental data and is applicable only to systems with N = 2 and whose formation curves are symmetrical about the mid point.

9. Least-square method.[14]

eq.(51) for N = 2 may be written in the following linear form ……

$$\frac{\bar{n}}{[\bar{n}-1]}\frac{1}{[L]} = \frac{2-\bar{n}}{\bar{n}-1}[L]K_1K_2 - K_1 \qquad \text{---------- (59)}$$

Eq. (57) is an equation of a straight line having slope of K_1K_2 and the intercept - K_1. It is not convenient to plot $\bar{n}/\bar{n}$-1. [L] against (2-$\bar{n}$)[L] / ($\bar{n}$-1) to obtained the straight line, as often happens, [L] varies over several powers often. Therefore it is better to evaluate the constants by the methods of least squate14. This method uses all the experimental data except the between $\bar{n}$ = 0.95 and $\bar{n}$ = 1.05. The constants were evaluated by the method of least square[14] described in *"study projects in physical chemistry"* by F.C. condon (Academic Press. (1963). p. 77) the values of K_1K_2 should be substituted into equation (57) to give a series of individual values of K_1.

10. Methods of Hearon and Gilbert.[3]

Hearon and Gilbert have suggested the following methods for point wise calculation of K_1 and K_2.

i) Here $\beta_2 = K_1K_2$ is obtained graphically from number of independent experiments. K_1 is then calculated at several points using eq.(17) in the form….

$$K_1 = \frac{(2-\bar{n}).K_1K_2[L]-\bar{n}}{(\bar{n}-1).[L]} \qquad \text{---------- (60)}$$

and averaged. The method requires a large number of titration curves to be determined for the system.

ii) This is reverse of method (1). Here K_1 is obtained from……

$$[L]\to 0\left\{\frac{\bar{n}}{L}\right\} = K_1 \qquad \text{---------- (61)}$$

and point wise calculation of K_2 is made using the relation.

$$K_1K_2 = \frac{K_1[L]-\bar{n}(1+K_1[L])}{(\bar{n}-2).[L]} \qquad \text{---------- (62)}$$

The method is open to objections involved in the use of eq. (61)

The choice of method for calculating stability constants depends on the complexity of the system, which can often be judjed from the shape of the formation curve. Irving and Rossoti [9] suggested recalculation of $\bar{n}$ from experimental values of pL and the calculated values of K_n using relation -

$$\bar{n}cal. = \frac{K_1[L] + 2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2} \qquad \text{---------- (63)}$$

Standard deviation, given by,

$$S = \{(\Delta/n)^2/ \text{ no. of observations}\}^{1/2} \qquad \text{---------- (64)}$$

Where $\bar{n}$ = $\bar{n}$ exp. - $\bar{n}$ cal. is determined to check the validity of the constants. The standard deviation should be as small as possible.

Gryder[15] has introduced that the values of the stability constants obtained may be checked by substitution into the appropriate determinant derived from eq. (18).

Limitations to applicability of computation methods:

The assumptions made in deriving the formation function *viz*. absence of metal ion hydrolysis, polynuclear complex formation, anion-complexing etc. sets limits to the applicability of computation methods described above in addition to those arising from the particular conditions under which the methods hold accordingly, the methods for detecting the presence of these neglected factors and also correction for them, if possible have been suggested by some workers.

Irving and Rossotti[9] associated the absence of perfect symmetry about the mid-point of the formation curve with the presence of polynuclear species formation of several types of complexes when ligands have several co-ordinations sites and with incomplete formation of one of the complexes. The symmetry of the formation curve therefore can be of great value in revealing such factors.

Rossotti and Rossoti[12] have suggested that $\bar{n}$ would be independent of T_M in

absence of polynuclear complex formation. Where only one polynuclear complex formation. Where only one polynuclear species is formed, determinations of $\bar{n}$ at different values of T_M and then extrapolation to low values of T_M have been recommended.

Mathematical methods of computing mononuclear stability constant, even when polynuclear species are present, have been suggested [16,17] but these seem to have been applied only to complexes arising in the metal ion hydrolysis.

Metal ion hydrolysis, if it occurs in the pH range of complex formation would result in higher than the true values of stability constants. Fraiser et. al.[18] studied hydrolysis of several bivalent metal ions in dioxane-water and have shown that, for these ions, computations made in the pH range 3-6 are least deviated by metal ion hydrolysis. Use of high ligandmetal ratio has been recommended to depress the pH range of complex formation if necessary.

We have studied the proton ligand stability constants and metal ligand stability constants at $30^0 \pm 0.2^0$C for four ligands by Calvin-Bjerrum titration technique adopted by Irving and Rossotti.[4]

The ligands selected are as under :

(1) 3-[{3-(2'-chloro)phenyl}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-AX)

(2) 3-[{3-(4'-chloro)phenyl}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-BX)

(3) 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-DY)

(4) 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-EY)

From the potentiometric titration reading of (i) acid (ii) acid + ligand (iii) acid + ligand + metal ion, system are summarized in Table - A-I, B-I, D-I, E-I on page 157, 168, 179, 190. The titration curves were obtained plotting pH meter reading versus volume of alkali added as shown in figures A-1(X), B-1(X), D-1(X) & E-1(X) on page 163, 174, 185, 196.

Calculation $\bar{n}_A$, $\bar{n}$ and pL:

From the titration curves $\bar{n}_A$, $\bar{n}$ and pL were calculated using the formula of Irving and Rossotti discussed on page 136. They are summarized in table A- II to A-VI, B-II to B-VI, D-II to D-VI and E-II to E-VI on page 158-162, 169-173, 180-184, 191-195.

Formation Curves:

The proton-ligand formation curves were obtained on plotting $\bar{n}_A$ versus pH {fig. A-2(Y), B-2(Y), D-2(Y) & E-2(Y)} on page 164, 175, 186, 197 and metal ligand formation curve were obtained on plotting $\bar{n}$ versus pL {fig. A-3, B-3, D-3 and E-3} on page 165, 176, 187, 198.

Determination of proton-ligand stability constants (^pK_nH) and Metal-ligand stability constant ($\log k_1$ and $\log k_2$).

The stepwise stability constatnts are obtained by interpolation and half $\bar{n}$ values method using proton-lignad formation curves. The results are summarized in Table -I on page 146.

Table - I

Proton-ligand stability constants of the ligands at $30^0 \pm 0.2^0$C

Ligand	$\log {}^{p}K_1{}^{H}$	$\log {}^{p}K_2{}^{H}$	$\log\beta H$
Chal AX	11.02	3.58	14.60
Chal BX	11.98	3.27	14.25
Chal DY	11.10	3.45	14.55
Chal EY	11.00	3.76	14.76

The Metal-ligand stability constants are presented in Table-II to VII on page 146 to 150.

a. Interpolation at half $\bar{n}$ values.

b. Half-integral method.

c. Linear plots method.

d. Mid point slope method.

f. Least square method.

Table - II
Proton-ligand stability constants of M(Chal AX) $30^0 \pm 0.2^0$C

Complexes	Stability constants	Computationals methods				
		a	b	c	d	e
$Cu(Chal\ AX)_2$	$\log K_1$	11.08	11.09	11.10	11.07	11.11
	$\log K_2$	10.52	10.55	10.54	10.50	10.53
	$\log \beta_2$	21.60	21.64	21.64	21.57	21.64
$Ni(Chal\ AX)_2$	$\log K_1$	10.78	10.77	10.80	10.81	10.78
	$\log K_2$	9.83	9.84	9.85	9.84	9.86
	$\log \beta_2$	20.61	20.63	20.65	20.65	20.64
$Co(Chal\ AX)_2$	$\log K_1$	10.41	10.42	10.40	10.43	10.41
	$\log K_2$	9.50	9.49	9.52	9.53	9.55
	$\log \beta_2$	19.91	19.91	19.92	19.96	19.96
$Fe(Chal\ AX)_2(H_2O)_2$	$\log K_1$	10.00	10.01	10.03	10.00	10.04
	$\log K_2$	9.29	9.30	9.21	9.31	9.33
	$\log \beta_2$	19.29	19.31	19.24	19.31	19.37

Table - III
Proton-ligand stability constants of $M(Chal\ BX)_2$ $30^0 \pm 0.2^0C$

Complexes	Stability constants	Computationals methods				
		a	b	c	d	e
$Cu(Chal\ BX)_2$	$\log K_1$	10.50	10.51	10.54	10.52	10.53
	$\log K_2$	9.61	9.60	9.63	9.62	9.61
	$\log \beta_2$	20.11	20.11	20.17	20.14	20.14
$Ni(Chal\ BX)_2$	$\log K_1$	10.12	10.11	10.13	10.14	10.12
	$\log K_2$	9.23	9.22	9.24	9.25	9.23
	$\log \beta_2$	19.35	19.33	19.37	19.39	19.35
$Co(Chal\ BX)_2$	$\log K_1$	10.77	10.78	10.76	10.77	10.79
	$\log K_2$	8.68	8.65	8.68	8.66	8.67
	$\log \beta_2$	19.45	19.43	19.44	19.43	19.46
$Fe(Chal\ BX)_2(H_2O)_2$	$\log K_1$	9.41	9.42	9.45	9.43	9.44
	$\log K_2$	8.40	8.41	8.42	8.40	8.43
	$\log \beta_2$	17.81	17.83	17.87	17.83	17.87

Table - V
Proton-ligand stability constants of $M(Chal\ DY)_2$ $30^0 \pm 0.2^0C$

Complexes	Stability constants	Computationals methods				
		a	b	c	d	e
$Cu(Chal\ DY)_2$	$logK_1$	11.10	11.11	11.12	11.09	11.13
	$logK_2$	10.05	10.04	10.07	10.06	10.08
	$logb_2$	21.15	21.15	21.19	21.15	21.21
$Ni(Chal\ DY)_2$	$logK_1$	10.72	10.70	10.73	10.71	10.74
	$logK_2$	9.60	9.61	9.59	9.62	9.63
	$logb_2$	20.32	20.31	20.32	20.33	20.37
$Co(Chal\ DY)_2$	$logK_1$	10.40	10.39	10.41	10.42	10.44
	$logK_2$	9.38	9.40	9.37	9.39	9.42
	$logb_2$	19.78	19.79	19.78	19.81	19.86
$Fe(Chal\ DY)_2(H_2O)_2$	$logK_1$	10.22	10.21	10.22	10.23	10.24
	$logK_2$	9.18	9.19	9.22	9.23	9.21
	$logb_2$	19.40	19.40	19.44	19.43	19.45

Table - VI

Proton-ligand stability constants of $M(Chal\ EY)_2$ $30^0 \pm 0.2^0C$

Complexes	Stability constants	Computationals methods				
		a	b	c	d	e
$Cu(Chal\ EY)_2$	$logK_1$	11.65	11.64	11.66	11.65	11.67
	$logK_2$	10.88	10.85	10.88	10.86	10.87
	$logb_2$	22.53	22.49	22.54	22.51	22.54
$Ni(Chal\ EY)_2$	$logK_1$	11.32	11.33	11.34	11.34	11.35
	$logK_2$	10.62	10.61	10.62	10.63	10.64
	$logb_2$	21.94	21.94	21.98	21.97	21.99
$Co(Chal\ EY)_2$	$logK_1$	11.02	11.02	11.04	11.00	11.03
	$logK_2$	10.10	10.11	10.12	10.14	10.13
	$logb_2$	21.12	21.13	21.16	21.14	21.16
$Fe(Chal\ EY)_2(H_2O)_2$	$logK_1$	10.40	10.41	10.43	10.42	10.39
	$logK_2$	9.38	9.39	9.38	9.40	9.41
	$logb_2$	19.78	19.80	19.81	19.82	19.80

EXPERIMANTAL

A. Copper nitrate (0.1 M):

Approximate 6.05g copper nitrate ($Cu(NO_3)_2$]$3H_2O$ B.D.H. analar quality was dissolved in 250ml distilled water (stock solution).

Standardization:[19]

25.0ml copper nitrate solution was diluted to 50.0 ml and 5.0ml concentrated ammonia solution and 5 to 6 drops of the indicator Fast sulphone Black-F was added. This solution was titrated against standard EDTA (0.1M., 37.225g. in 1L.) solution (colour change blue to dark green).

The volume of 0.1M EDTA used was 25.1ml., 25.0ml. copper titrate = 25.1ml 0.1M EDTA. Strength of copper nitrate solution = 0.1004 M Cu(II).

1.0ml, 0.1M EDTA = 6.354mg. Cu(II), 99.60ml., 0.1004M copper nitrate solution was diluted to 100ml with distilled water to get 0.1M solution.

B. Nickel Nitrate (0.1M):

Approximately 7.3g Nickel Nitrate [$Ni(No_3)_2$, $6H_2O$, B.D. H.analar quality] was disslove in 250ml. distilled water (stock solution).

Standardization:[19]

25.0ml nickel solution was diluted to 50.0 ml and 10 of buffer solution (1.0M. ammonia + 1.0M ammonium chloride and 10 to 15 drops of indicator bromopyrogallol red (in 50% ethanol) was added. It was titrated against 0.1M EDTA solution, colour change blue to wine red.

The volume of 0.1M EDTA used was 25.2 ml. 25.0 ml. Nickel nitrate = 25.2ml. 0.1M EDTA. Strength of nickel nitrate solution = 0.1008 M Ni (II) [1ml, 0.1M EDTA = 5.871gm. Ni(II)]. 99.21ml. 0.1008M nickel nitrate solution was

diluted to 100ml with distilled water to get 0.1M solution.

C. Cobalt nitrate (0.1M):

Approximately 7.3g cobalt nitrate [$Co(NO_3)_2$. $6H_2O$ B.D.H. analar quality] was dissolve in 250 ml. distilled water (stock solution).

Standardization:[19]

25.0ml of stock solution $Co(NO_3)_2$. $6H_2O$ was diluted to 100ml. and three drops of the indicator xylenol orange (in distilled water) was added followed by very dilute sulphuric acid drops wise until the colour of the solution just changes from red to yellow. Then powedered hexamine was added with shaking until the deep red colour was restored (pH = 6.0). The solution was warmed to 40^0C and titrated against standard 0.1M EDTA solution drop wise (colour change red yellow orange).

The volume of 0.1M EDTA used was 25.0ml. cobalt nitrate solution = 25.4ml. 0.1M EDTA strength of cobalt nitrate solution = 0.1016M. Co(II). [1.0ml., 0.1M EDTA = 5.894mg. Co(II)] 98.43ml. 0.1016M cobalt nitrate solution was diluted to 100ml. with distilled water to get 0.1M solution.

D. Ferrous ammonium sulphate (0.1M):

Approximately 9.8g ferrous ammonium sulphate B.D.H. analar was dissolved in distilled water and treated with sodium hydroxide solutions. The hydroxide was dissolved by adding minimum amount of dil. Nitric acid drop wise and the solution so prepared was diluted to 250 ml. with distilled water.

Standardization:

Reagent : $KMnO_4$ solution

Indicator : Self indicator

25.0ml of the Ferrous solution was taken in a conical flask and 25.0ml of H_3PO_4 was added. It was titrated against standard permanganate solution till faint pink colour persists.

25.0 ml. of 0.1 M $KMnO_4$ solution was required 25.0 ml of ferrous solution. Hence the strength of the solution was 0.01M.

[1.0ml. 0.1 $KMnO_4$ = 0.0558g Fe(II)]

EDTA solution (0.1M):

37.225g. disodium dihydrogen ethylenediamine tetra acetate was dissolved in distilled water and diluted to one litre to prepare 0.1 M EDTA solution.

INDICATOR:

(i) Fast sulphon black - F:

0.5% aqueous solution of fast sulphon black-F was prepared.

(ii) Bromopyrogallol red:

0.05g. of bromopyrogallol red was dissolved in 100ml of 50% ethanol.

(iii) Xylenol orange:

0.5g of xylenol orange was dissolved in 100ml. of distilled water.

Preparation of nitric acid solution (0.1M):

20.0ml (Sp.G., 1.42) of concentrated nitric acid (B.D.H. analar) was diluted to 250 ml. with distilled water to get stock solution of nitric acid. A. 10.0 ml. of solution A was diluted to 100 ml. to get solution B. 10ml. of B was titrated potentiometrically against standard 0.1M sodium hydroxide solution. The volume of alkali used for neutralization was obtained graphically. It was 10.0 ml.

10.0 ml. HNO_3 solution = 10.1 ml. 0.1M NaOH

Molarity of solution B = 0.101M

Molarity of solution A = 1.01M

99.01 ml. of solution A was diluted to 100ml. with distilled water to get 0.1M HNO_3 solution. Its strength was again verified by titrating it potentiometrically against 0.1M NaOH solution.

Preparation of NaOH solution (0.5M, 0.1M):

Carbonate free sodium hydroxide solution was prepared by dissolving 20.2g. Sodium hydroxide pallets (NaOH B.D.H. Analar) in carbon dioxide free distilled water and diluted to one litre. Its strength was determined potentiometrically by titrating it (10.0 ml. diluted to 50.0 ml.) against standard 0.05M succinic acid solution. Then the stock solution was suitably diluted as to obtain 0.5M and 0.1M NaOH solutions.

Sodium nitrate solution (1.0M) :

21.25g. of sodium nitrate ($NaNO_3$, B.D.H. Analar) was dissolved in distilled water and it was diluted to 250 ml. to get 1.0M $NaNO_3$ solution.

Dioxane (diethylene dioxide):

Guaranteed reagent of S.Merck was purified by the method described by Vogel.[20] The freezing point and boiling point of purified solvent was about 11.7^{0}C and 101-102^{0}C respectively. The purified solvent was stored in amber coloured tightly stopped bottles.

Ligand solution for the pH titration :

0.1M solution of the lignad was prepared in purified dioxane.

Buffer solutions for the calibration of pH meter:

i) 0.05M potassium hydrogen phthalate buffer:

Potassium hydrogen phthalate ($KHC_8H_5O_4$, B.D.H. analar Mol. Wt. 204.22g.) was dired at 120^{0}C and cooled, 10.21g. of the solid was dissolved in distilled water and diluted to one litre. A fresh buffer solution was always prepared every week. Few drops of toluene were added as a preservative. It was kept in a pyrex flask.

ii) 0.01M Borax buffer:

3.81g of Borax ($Na_2B_4O_7$. $10H_2O$, B.D.H. Analar) was dissolved in carbon dioxide free water and diluted to one litre. It was kept in a corning flask and was protected from exposure to atmosphere carbon dioxide and was replaced every week.

pH meter accessories:

A systronic expanded scale pH meter of wide pH range (0.0 to 14.0 and on expanded scale with minimum measurable pH change of 0.01) was employed for the pH determination. The systronic glass electrode of pH range 0 to 14 as indicating electrode and a saturated calmoal electrode as a reference electrode were used. Before operation, the glass electrode was immersed in 0.1M HCI for twenty minutes. Then it was washed thoroughly with distilled water.

Calibration of the pH meter:

Before starting the pH titrations the pH meter was calibrated with buffer solution of known pH. The buffer solution was taken in a beaker immersed in an electrically heated automatic temperature controlled thermostat. When it attained a constant temperature, the glass electrode and the calomel were immersed in it, and the pH meter pointer already set for zero was set at a value of the pH of the buffer solution. 0.05M potassium hydrogen phthalate solution was used as the fixed standard and it accuracy in the alkaline range was checked with 0.01M Borax solution.

The exact pH values of three buffers at different temperature recorded from the literature[21] are given in theoretical part II on page 138.

Calvin Bjerrum pH titrations:

The following sets of the mixtures were prepared for titration:

1) 0.8ml. HNO_3 (1.0M)+ 11.2ml. water + 24.0 ml dioxane + 4.0ml. $NaNO_3$ (1.0M).
2) 0.8ml. HNO_3 (1.0M)+ 11.2ml. water + 22.0 ml dioxane + 2.0 ml. ligand solution (0.1M) + 4.0ml. $NaNO_3$ (1.0M).
3) 0.8ml. HNO_3 (1.0M)+ 10.8ml. water + 22.0 ml dioxane + 2.0 ml. ligand solution (0.1M) + 0.4 ml. metal solution + 4.0ml. $NaNO_3$ (1.0M).

The total volume V^0 in each set was 40.0 ml., keeping constant temperature $t = 30^0 \pm 0.2^0$ C and dioxane : water :: 60 : 40 (v/v).

[A] pH metric titration of 3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-AX) and with methyl ions at $30^0 \pm 0.2^0$ C.

i) Titration of the acid mixture No. 1

Mixture No.1, as mentioned earlier was taken in the titration vessel and when it attained a constant temperature, it was titrated against standard alkali solution (0.5M). The change in the pH of the solution with each addition of alkali was recorded. It was mentioned in Table-A-I on page 157.

ii) Titration of the mixture No.2 containing acid and ligand:

Mixture No.2, as mentioned earlier was taken in the clean titrating beaker and when it attained the same constant temperature, it was titrated as above. The change in the pH was recorded as in Table A-I on page 157.

iii) Titration of the mixture No. 3 containing acid, ligand and metal ion:

Mixture No.3 as mentioned earlier was taken in the clean ititrating beaker and when it attained the same constant temperature, it was titrated as above. The change in the pH was recorded as in Table A-I on page 157.

The metal ions selected for our study were Cu(II), Ni(II), Co(II) and Fe(II) presented in chapter-II to V. The titrations were carried out at $30^0 \pm 0.2^0$C. During the titration, the change in colours and appreance of turbidity at particular pH value were recorded simultaneously.

Table : A-I
The pH titration reading of acid, acid + ligand (Chal AX) and acid + ligand (Chal AX) + metal ion.

N^0 = 0.5M, E^0 = 0.02M. V^0 = 40.0ml

T^0_L = 5 x 10-3M T^0_M = 1 x 10-3M t = $30^0 \pm 0.2^0$C,

u^0 = 0.1M.

Solvent = Dioxane : Water :: 60 : 40 (v/v)

Vol. of Alkali added.	Acid	Acid + ligand.	pH meter reading (B)			
			Acide + ligand (Chal AX) + metal ion:			
			Cu^{+2}	Ni^{+2}	Co^{+2}	Fe^{+2}
0.00	1.51	1.51	1.51	1.51	1.51	1.51
0.50	1.66	1.78	1.81	1.83	1.83	1.85
1.00	1.87	2.41	2.52	2.48	2.54	2.58
1.10	1.92	2.58	2.72	2.65	2.86	2.95
1.20	2.00	2.81	3.00	2.93	3.08	3.18
1.30	2.06	3.16	3.35	3.27	3.47	3.56
1.40	2.24	3.75	3.82	3.78	3.86	3.92
1.50	2.40	4.53	4.41	4.28	4.53	4.64
1.52	2.51	4.72	4.62	4.50	4.85	5.00
1.54	2.63	4.93	4.90	4.72	5.24	5.39
1.56	2.75	5.21	5.12	4.98	5.46	5.62
1.58	2.97	5.76	5.41	5.37	5.58	5.71
1.60	10.17	6.12	5.68	5.50	5.73	6.00
1.62	11.68	6.67	5.89	5.63	5.95	6.24
1.64	12.10	7.70	6.12	5.77	6.36	6.62
1.66	12.23	8.82	6.23	5.96	6.54	6.83
1.68	12.41	9.11	6.55	6.12	6.79	7.08
1.70	12.58	9.62	6.72	6.23	6.90	7.23
1.75	12.73	10.48	7.21	6.71	7.38	7.67
1.80	12.85	10.97	7.48	6.95	7.77	8.11
1.85	12.90	11.21	7.77	7.30	8.00	8.40
1.90	12.93	11.40	7.90	7.51	8.08	8.59

Table : A-II

3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one(Chal AX) at $30^0 \pm 0.2^0$ C.

B	V_2-V_1	$\bar{n}A$	$\log {}^{P}K_2{}^{H}$
2.25	-0.3865	1.9708	3.5825
2.50	-0.3674	1.9204	3.5862
2.75	-0.3316	1.8295	3.5818
3.00	-0.3141	1.7855	3.5835
3.25	-0.2645	1.6614	3.5846
3.50	-0.2230	1.5576	3.5846
3.75	-0.1873	1.4683	3.5811
4.00	-0.1431	1.3578	3.5850
4.25	-0.1126	1.2815	3.5818
4.50	-0.0918	1.2295	3.5862

B	V_2-V_1	$\bar{n}A$	$\log {}^{P}K_2{}^{H}$
9.00	0.0895	0.7761	11.0231
9.25	0.0934	0.7664	11.0215
9.50	0.0987	0.7532	11.0272
9.75	0.1146	0.7131	11.0233
10.00	0.1215	0.6962	11.0262
10.25	0.1405	0.6487	11.0211
10.50	0.1480	0.6300	11.0229
10.75	0.1662	0.5845	11.0240
11.00	0.1925	0.5188	11.0261
11.25	0.2498	0.3756	11.0245

Table : A-III

Copper+bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal AX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.00	0.0040	0.0500	11.9634
5.25	0.0138	0.1726	11.6830
5.50	0.0259	0.3239	11.4471
5.75	0.0436	0.5451	11.2185
6.00	0.0658	0.8225	10.9967
6.25	0.0923	1.1534	10.7830
6.50	0.1142	1.4268	10.5653
6.75	0.1404	1.7539	10.3573
7.00	0.1505	1.8798	10.1247

Table : A-IV

Nickel+bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal AX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.50	0.0108	0.1350	11.4297
5.75	0.0191	0.2388	11.1894
6.00	0.0310	0.3875	10.9534
6.25	0.0451	0.5636	10.7205
6.50	0.0593	0.7409	10.4885
6.75	0.0822	1.0268	10.2690
7.00	0.1019	1.2728	10.0470
7.25	0.1220	1.5237	9.8275
7.50	0.1538	1.9207	9.6286

Table : A-V

Cobalt+bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal AX) at $30^0 \pm 0.2^0$ C.

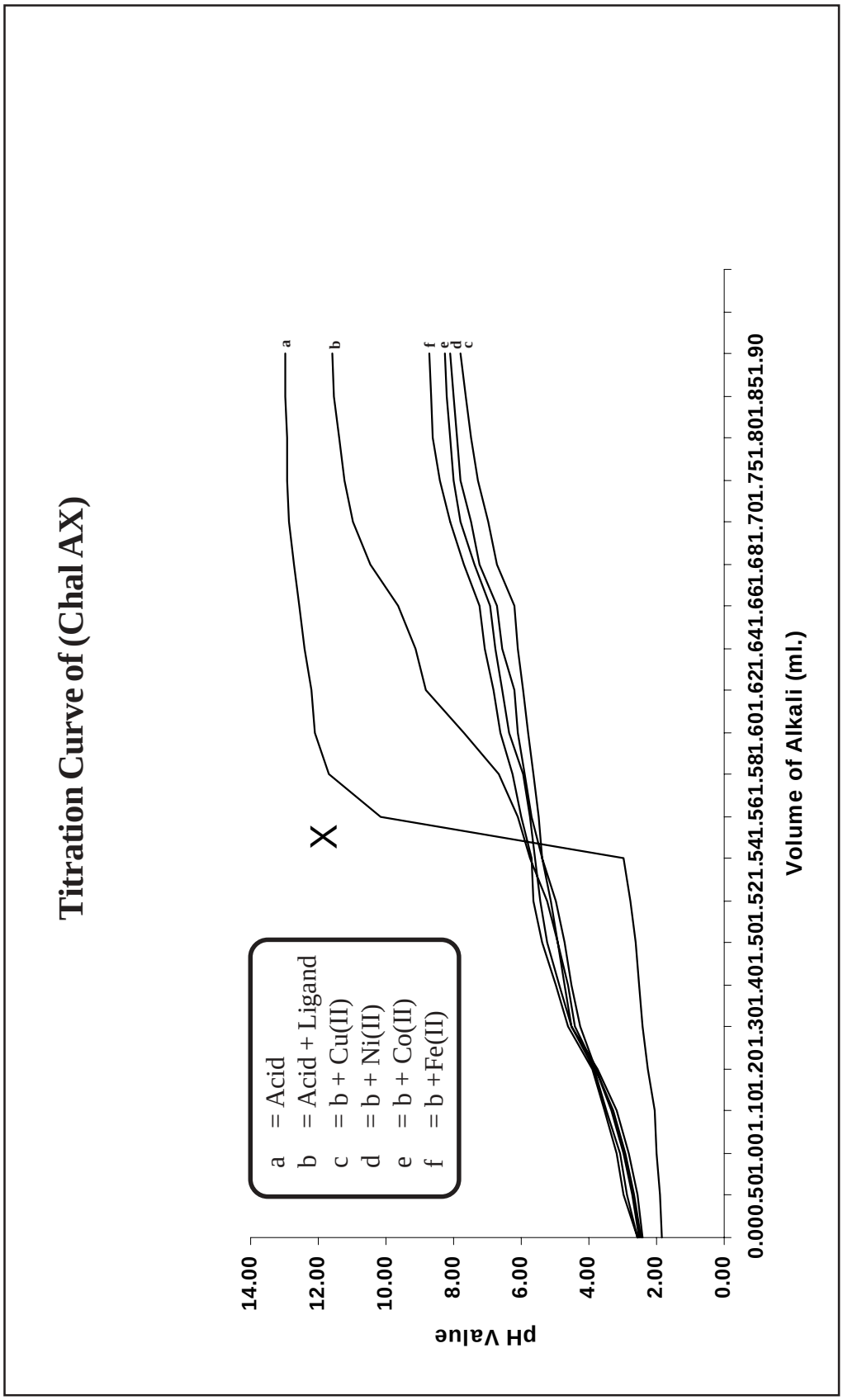
B	V_3-V_2	$\bar{n}$	$_pL$
5.75	0.0038	0.0475	11.1721
6.00	0.0071	0.0891	10.9259
6.25	0.0203	0.2536	10.6909
6.50	0.0388	0.4847	10.4629
6.75	0.0475	0.5933	10.2236
7.00	0.0716	0.8943	10.0047
7.25	0.1002	1.2574	9.7952
7.50	0.1216	1.5118	9.5790
7.75	0.1503	1.8768	9.3744

Table : A-VI

Iron+bis[3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal AX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	n	$_pL$
6.25	0.0102	0.1274	10.6794
6.50	0.0131	0.1636	10.4328
6.75	0.0302	0.3772	10.2027
7.00	0.0428	0.5346	9.9679
7.25	0.0678	0.8467	9.7497
7.50	0.0953	1.1901	9.5375
7.75	0.1226	1.5309	9.3285
8.00	0.1397	1.7441	9.1063
8.25	0.1594	1.9896	8.8907

Fig : A-I


Titration Curve of (Chal AX)
a = Acid
b = Acid + Ligand
c = b + Cu(II)
d = b + Ni(II)
e = b + Co(II)
f = b +Fe(II)
pH Value
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00 0.50 1.00 1.10 1.20 1.30 1.40 1.50 1.52 1.54 1.56 1.58 1.60 1.62 1.64 1.66 1.68 1.70 1.75 1.80 1.85 1.90
Volume of Alkali (ml.)

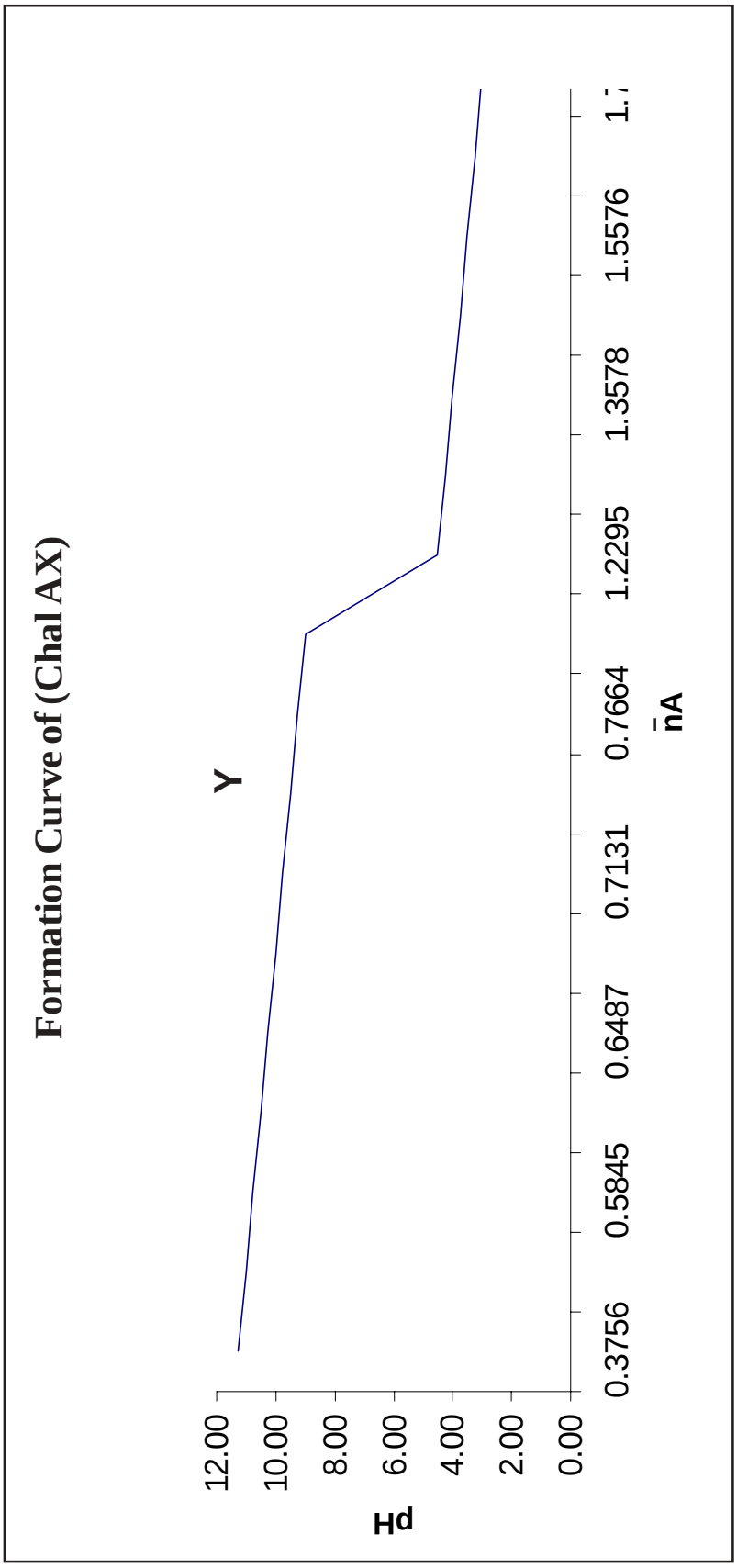

Formation Curve of (Chal AX)
Y
pH
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.3756
0.5845
0.6487
0.7131
0.7664
1.2295
1.3578
1.5576
n̄A

Fig.-A-2

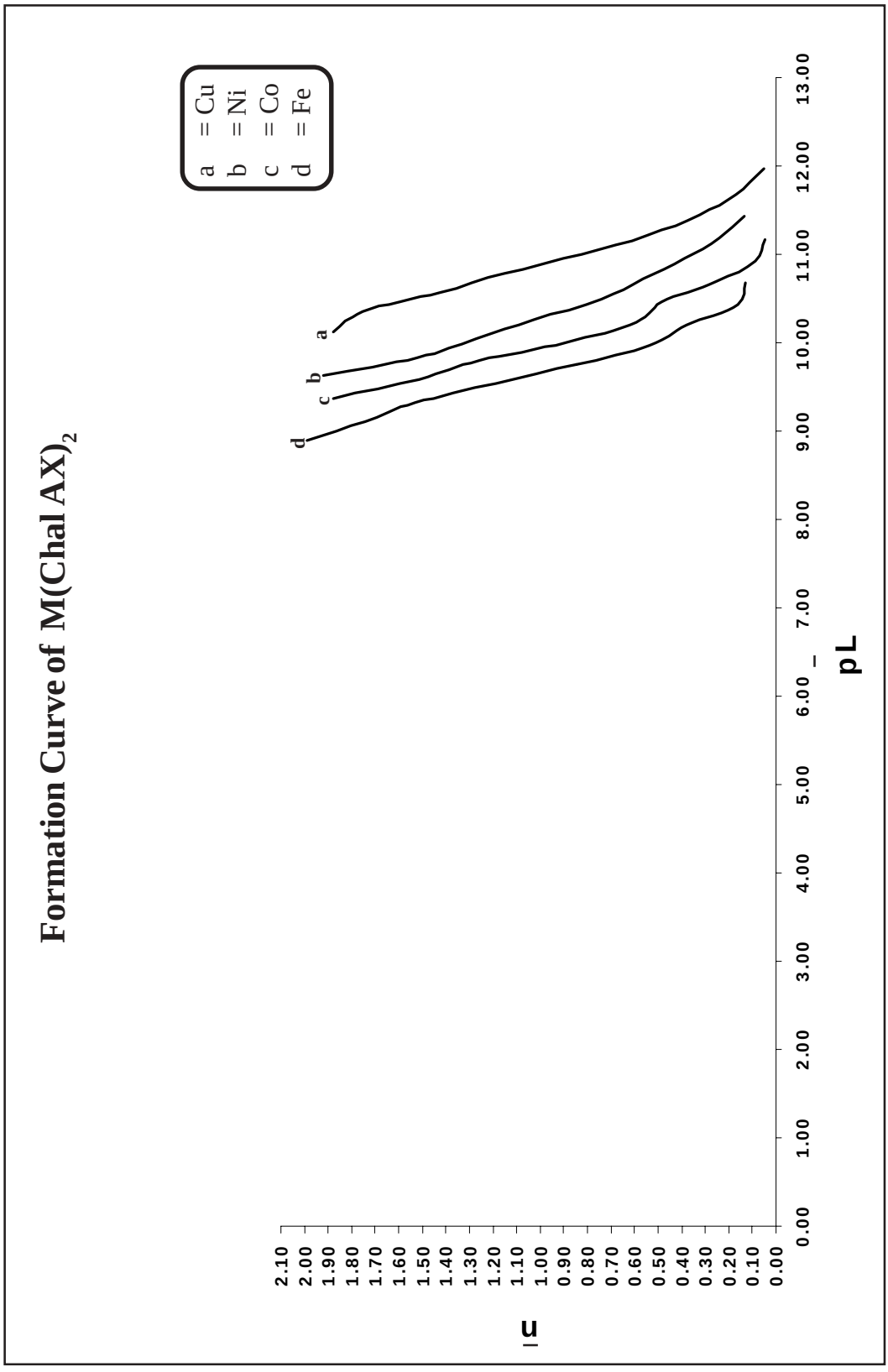

Formation Curve of M(Chal AX)2
a = Cu
b = Ni
c = Co
d = Fe
a
b
c
d
n̄
pL
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
1.30
1.40
1.50
1.60
1.70
1.80
1.90
2.00
2.10
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00

Fig.- A -3

Fig.- A-4
Linear Plot of Ligand Chal AX
Chal AX at $30^0 \pm 0.2^0$ C

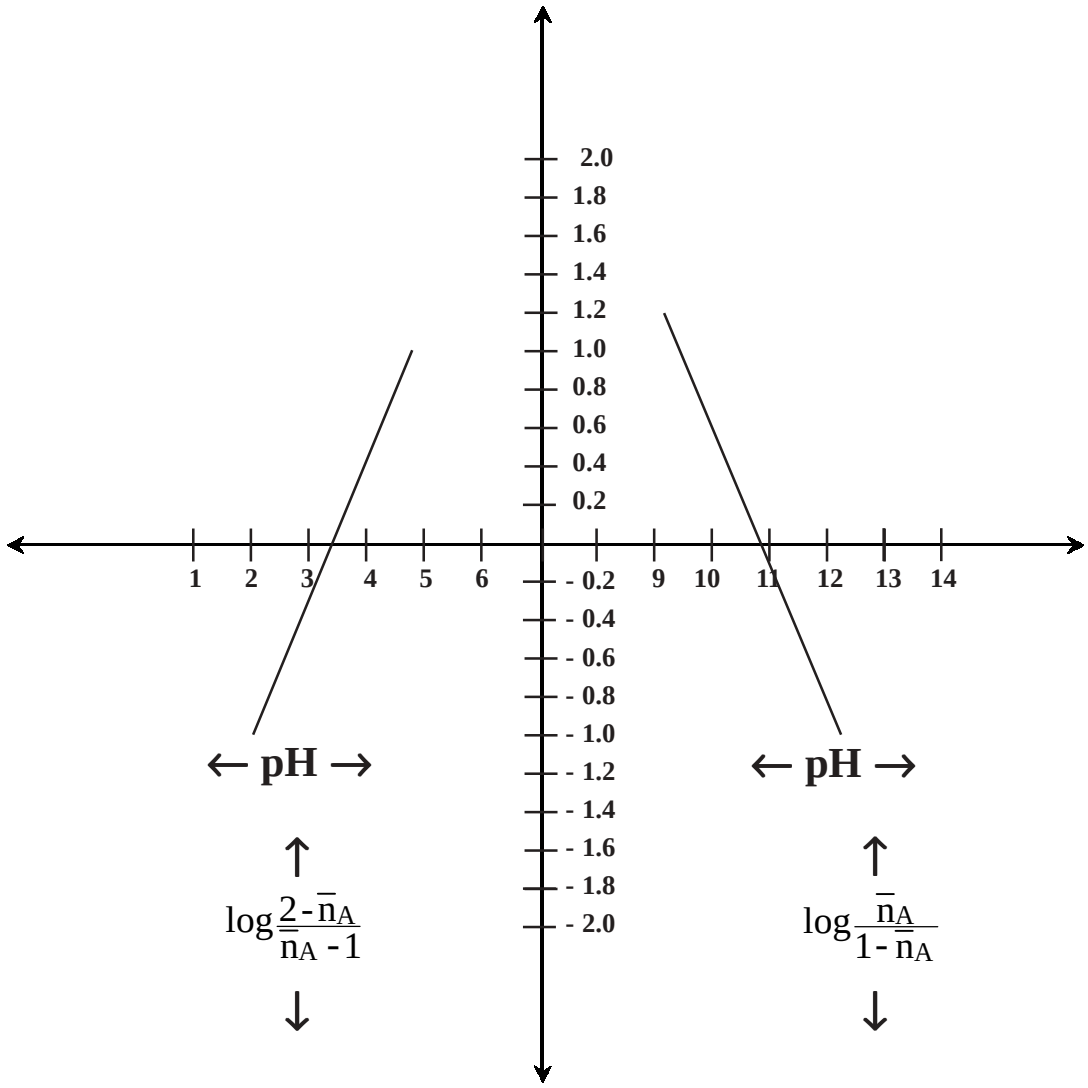


Fig.- A-5
Linear Plot of $M(Chal\ AX)_2$

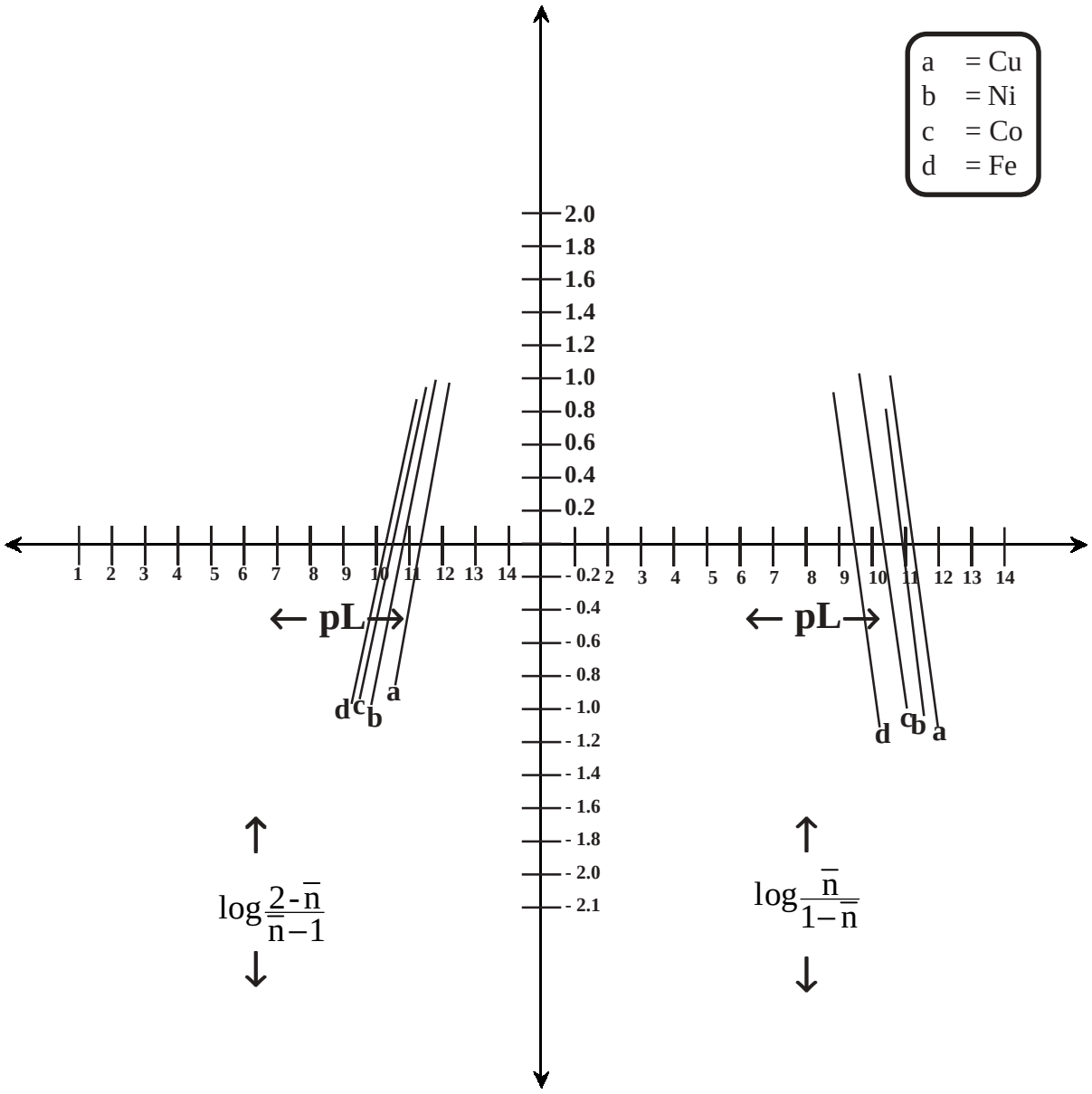


Table : B-I
The pH titration reading of acid, acid + ligand (Chal BX) and acid + ligand (Chal BX) + metal ion.

N^0 = 0.5M, E^0 = 0.02M. V^0 = 40.0ml

T^0_L = 5 x 10-3M T^0_M = 1 x 10-3M t = $30^0 \pm 0.2^0$C,

u^0 = 0.1M.

Solvent = Dioxane : Water :: 60 : 40 (v/v)

Vol. of Alkali added.	Acid	Acid + ligand.	pH meter reading (B)			
			Acide + ligand (Chal BX) + metal ion:			
			Cu^{+2}	Ni^{+2}	Co^{+2}	Fe^{+2}
0.00	1.51	1.51	1.51	1.51	1.51	1.51
0.50	1.66	1.75	1.81	1.82	1.83	1.85
1.00	1.87	2.16	2.20	2.21	2.22	2.48
1.10	1.92	2.30	2.41	2.48	2.58	2.92
1.20	2.00	2.51	2.72	2.88	3.32	3.72
1.30	2.06	2.76	3.17	3.56	3.78	5.00
1.40	2.24	3.33	4.08	4.80	5.12	5.97
1.50	2.40	4.89	5.21	5.39	5.51	6.12
1.52	2.51	5.41	5.41	5.52	5.64	6.33
1.54	2.63	5.93	5.63	5.70	5.82	6.48
1.56	2.75	6.52	5.85	5.97	6.24	6.71
1.58	2.97	7.29	6.07	6.38	6.52	7.00
1.60	10.17	7.80	6.24	6.49	6.79	7.22
1.62	11.68	8.72	6.35	6.72	7.02	7.45
1.64	12.10	9.26	6.52	6.96	7.28	7.62
1.66	12.23	8.65	6.84	7.18	7.52	7.82
1.68	12.41	10.00	7.00	7.28	7.76	8.08
1.70	12.58	10.21	7.26	7.51	8.15	8.41
1.75	12.73	10.75	7.63	7.80	8.53	8.71
1.80	12.85	10.89	8.03	8.12	8.72	9.11
1.85	12.90	11.12	8.11	8.25	8.93	9.30
1.90	12.93	11.31	8.21	8.42	9.07	9.42

Table : B-II

3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal BX) at $30^0 \pm 0.2^0$ C.

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
2.25	-0.3880	1.9745	3.2713
2.50	-0.3201	1.8019	3.2778
2.75	-0.3002	1.7510	3.2729
3.00	-0.2739	1.6850	3.2747
3.25	-0.1972	1.4931	3.2726
3.50	-0.1671	1.4178	3.2705
3.75	-0.1474	1.3686	3.2713
4.00	-0.1313	1.3183	3.2776
4.25	-0.1203	1.3008	3.2729
4.50	-0.1085	1.2713	3.2784

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
9.00	0.0415	0.8962	10.9872
9.25	0.0495	0.8762	10.9883
9.50	0.0529	0.8677	10.9889
9.75	0.0691	0.8272	10.9806
10.00	0.0815	0.7962	10.9868
10.25	0.1080	0.7300	10.9835
10.50	0.1229	0.6927	10.9811
10.75	0.1683	0.5792	10.9874
11.00	0.2025	0.4938	10.9825
11.25	0.2898	0.2756	10.9869

Table : B-III

Copper+bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal BX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.50	0.0007	0.0087	11.0680
5.75	0.0152	0.1903	10.8343
6.00	0.0298	0.3730	10.6014
6.25	0.0523	0.6545	10.3790
6.50	0.0718	0.8983	10.1543
6.75	0.0933	1.1672	9.9341
7.00	0.1151	1.4398	9.7164
7.25	0.1308	1.6362	9.4912
7.50	0.1517	1.8976	9.2765

Table : B-IV

Nickel+bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal BX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.75	0.0101	0.1264	10.8285
6.00	0.0142	0.1777	10.5833
6.25	0.0231	0.2890	10.3436
6.50	0.4100	0.5130	10.1156
6.75	0.0592	0.7406	9.8879
7.00	0.0781	0.9770	9.6629
7.25	0.1009	1.2662	9.4451
7.50	0.1192	1.4911	9.2233
7.75	0.1422	1.7787	9.0101

Table : B-V

Cobalt+bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal BX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
6.25	0.0095	0.1188	10.3280
6.50	0.0203	0.2539	10.0904
6.75	0.0318	0.3978	9.8540
7.00	0.0521	0.6517	9.6289
7.25	0.0680	0.8506	9.3994
7.50	0.0910	9.1383	9.1808
7.75	0.1101	1.3772	8.9588
8.00	0.1219	1.5248	8.7270
8.25	0.1385	1.7324	8.4956

Table : B-VI

Iron+bis[3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one] (Chal BX) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
6.50	0.0051	0.0638	10.0730
6.75	0.0112	0.1406	9.8300
7.00	0.0193	0.2414	9.5873
7.25	0.0411	0.5142	9.3652
7.50	0.0583	0.7293	9.1367
7.75	0.0821	1.0270	8.9184
8.00	0.1042	1.3034	8.6900
8.25	0.1189	1.4873	8.4723
8.50	0.1461	1.8262	8.2666

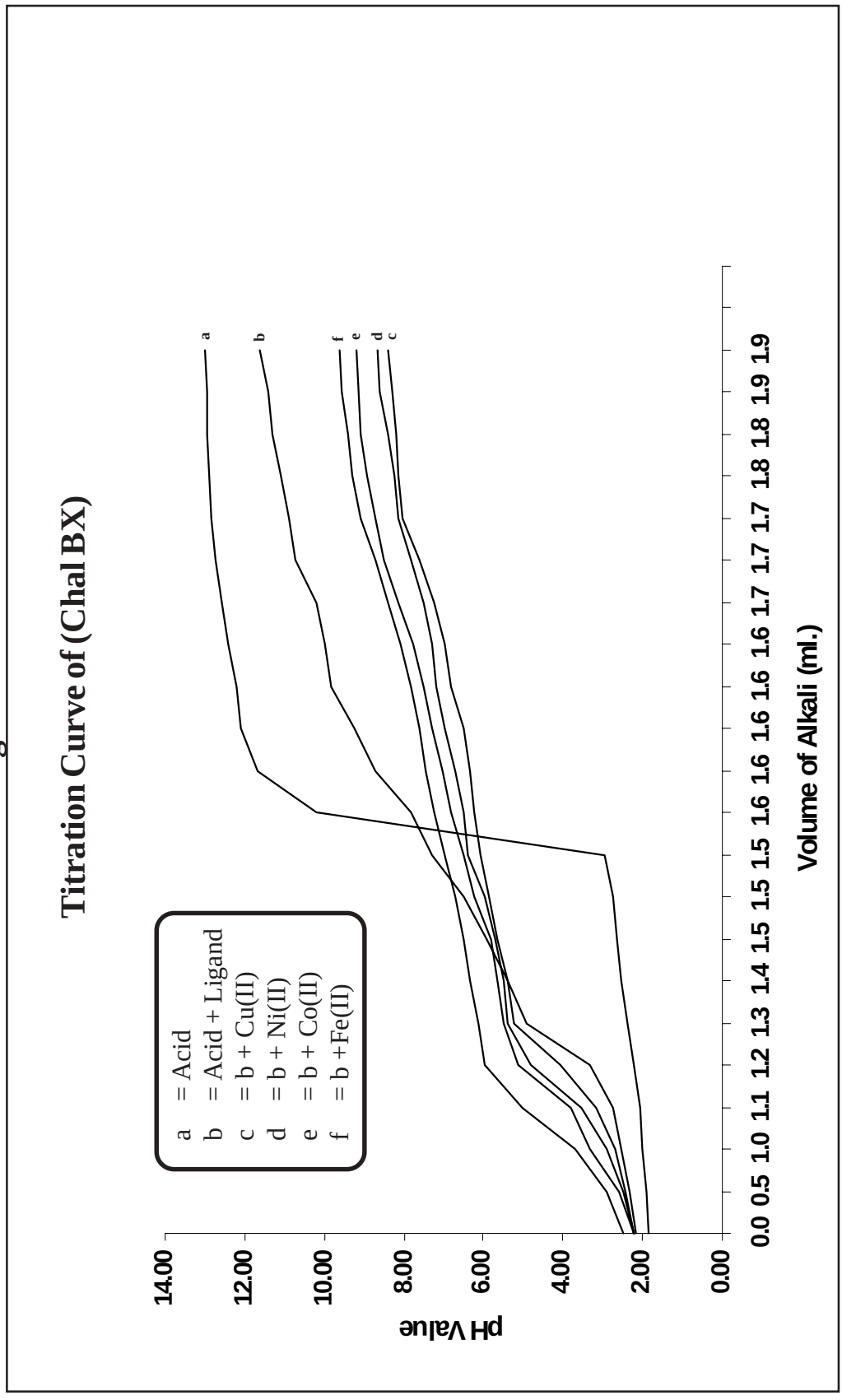

Titration Curve of (Chal BX)
a = Acid
b = Acid + Ligand
c = b + Cu(II)
d = b + Ni(II)
e = b + Co(II)
f = b +Fe(II)
pH Value
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.0 0.5 1.0 1.1 1.2 1.3 1.4 1.5 1.5 1.5 1.6 1.6 1.6 1.6 1.6 1.7 1.7 1.7 1.8 1.8 1.9 1.9
Volume of Alkali (ml.)
a
b
f
e
d
c

Fig. : B-I

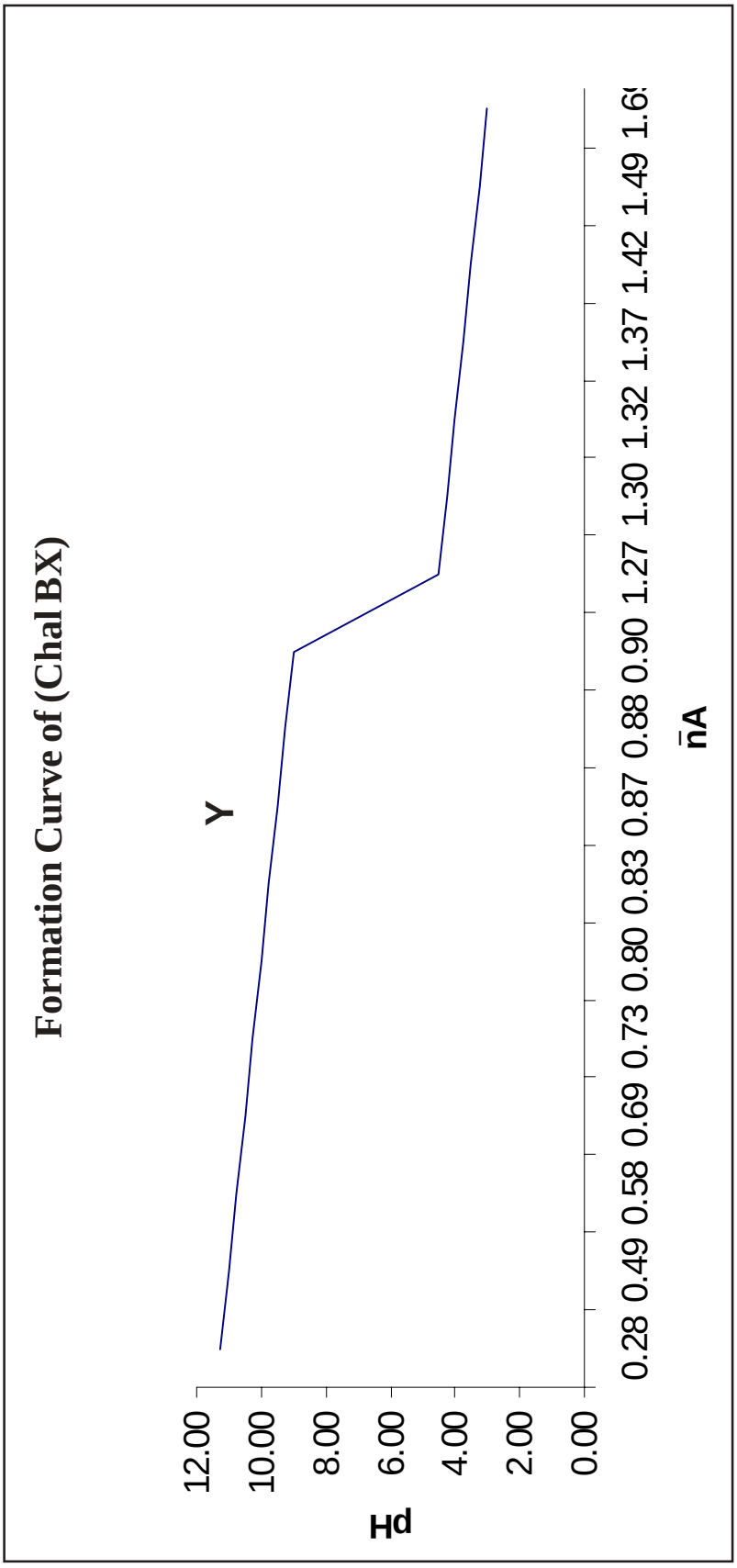

Formation Curve of (Chal BX)
Y
pH
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.28 0.49 0.58 0.69 0.73 0.80 0.83 0.87 0.88 0.90 1.27 1.30 1.32 1.37 1.42 1.49 1.6
n̄A

Fig.-B-2

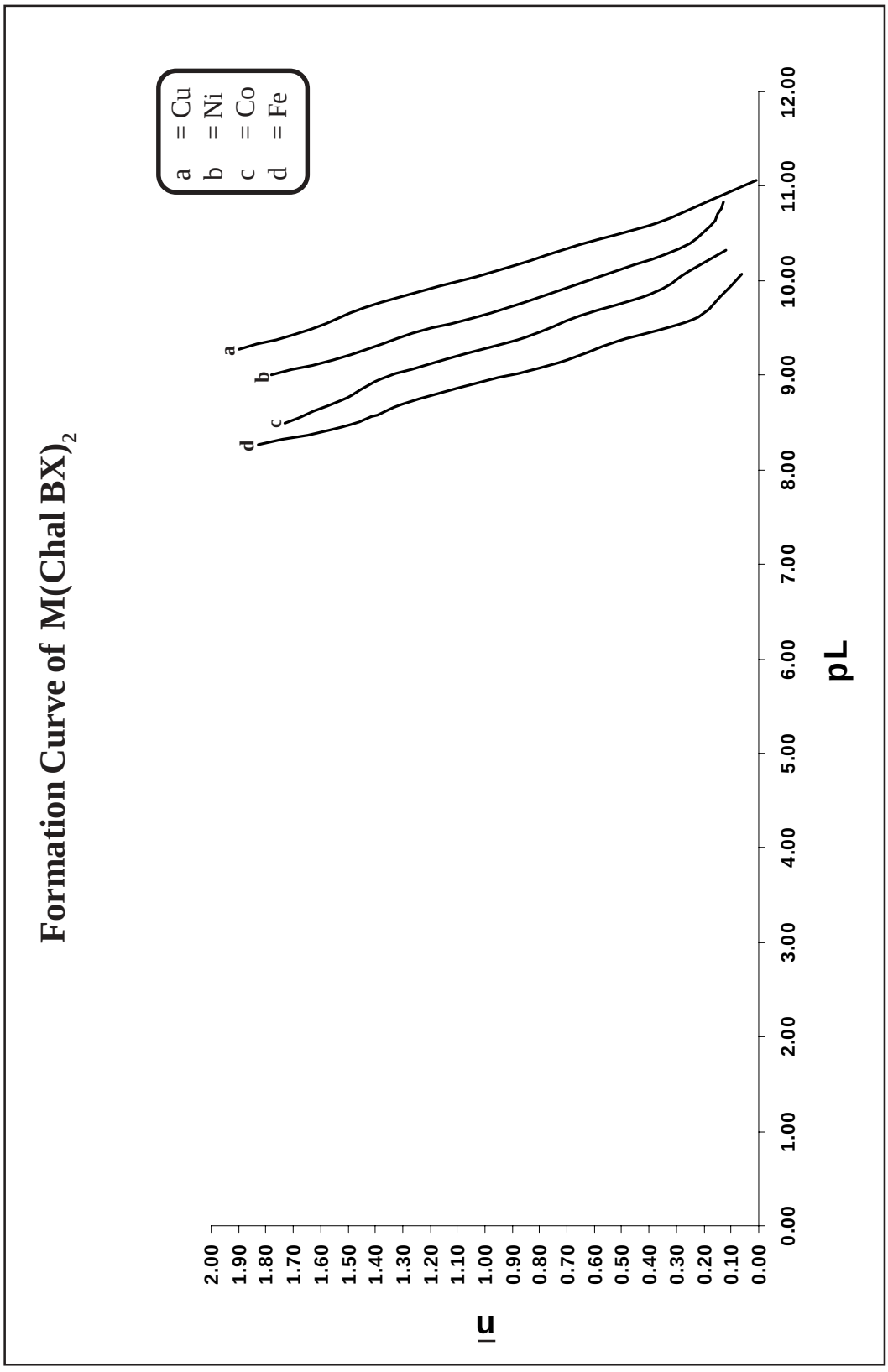

Formation Curve of M(Chal BX)2
a = Cu
b = Ni
c = Co
d = Fe
a
b
c
d
n̄
pL
2.00
1.90
1.80
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00

Fig.- B -3

Fig.- B-4
Linear Plot of Ligand Chal BX
Chal BX at $30^0 \pm 0.2^0$ C

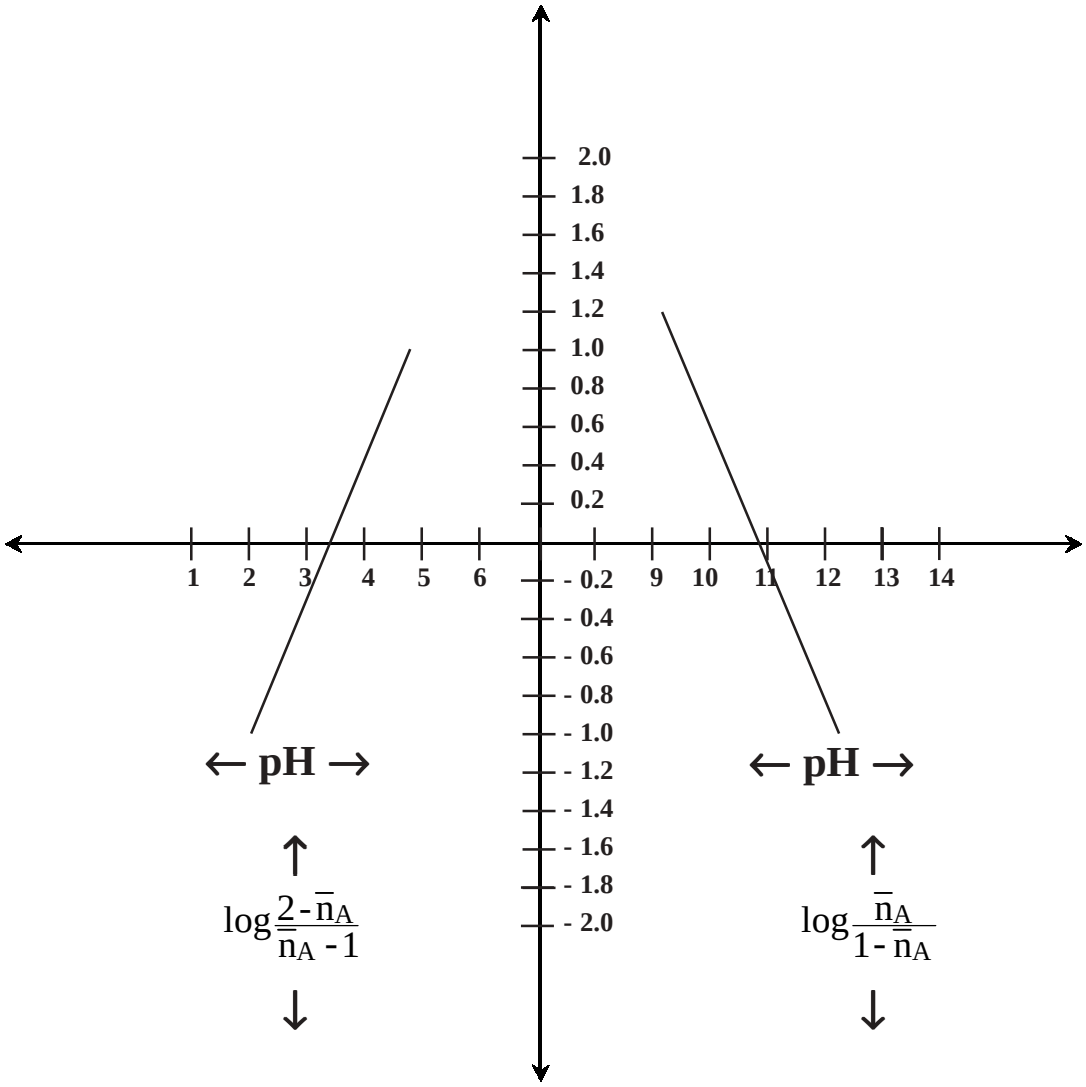


Fig.- B-5
Linear Plot of $M(Chal\,BX)_2$

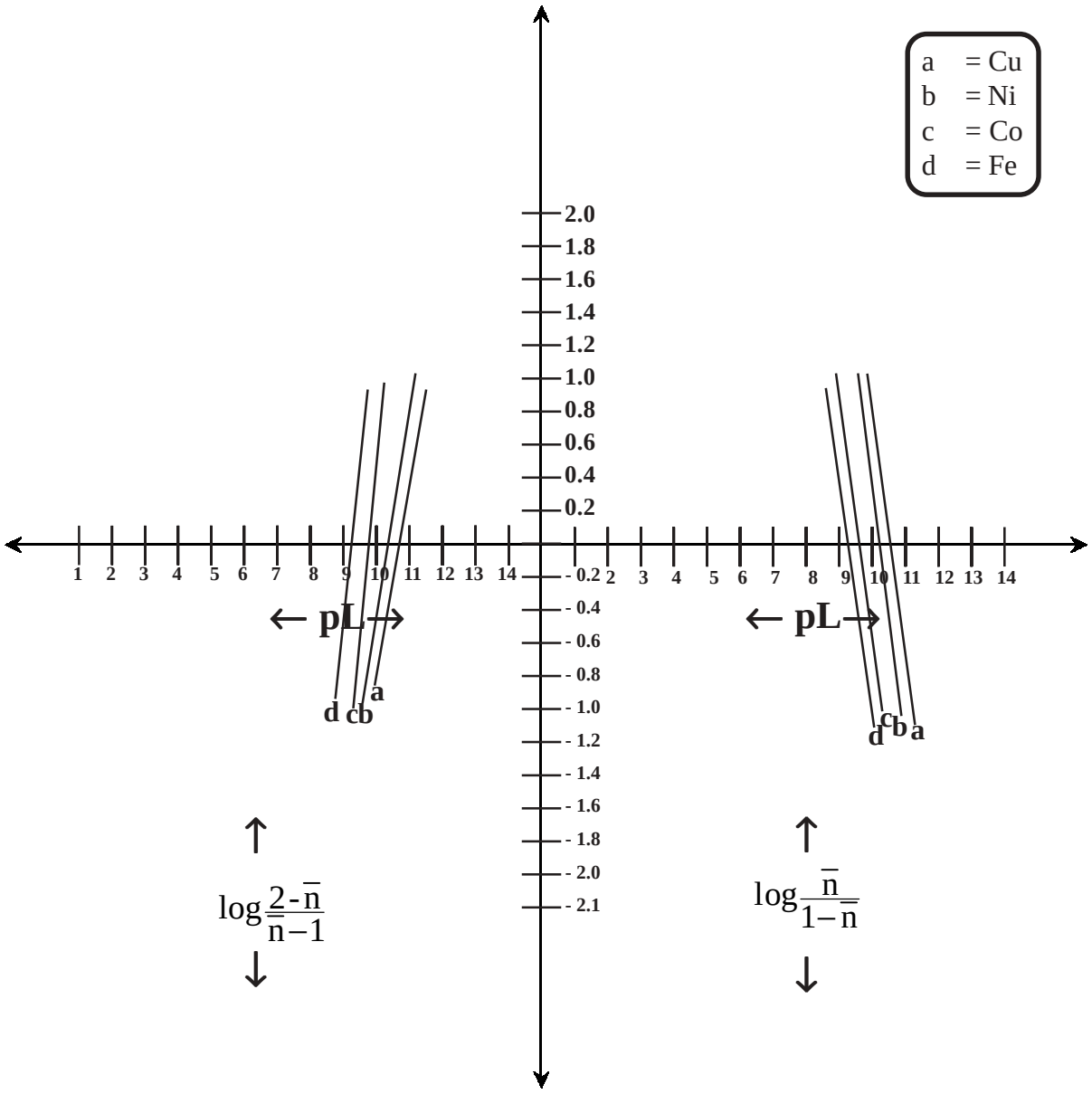


Table : D - I
The pH titration reading of acid, acid + ligand (Chal DY) and acid + ligand (Chal DY) + metal ion.

N^0 = 0.5M, E^0 = 0.02M. V^0 = 40.0ml

T^0_L = 5 x 10-3M T^0_M = 1 x 10-3M t = $30^0 \pm 0.2^0$C,

u^0 = 0.1M.

Solvent = Dioxane : Water :: 60 : 40 (v/v)

Vol. of Alkali added.	Acid	Acid + ligand.	pH meter reading (B)			
			Acid + ligand (Chal DY) + metal ion:			
			Cu^{+2}	Ni^{+2}	Co^{+2}	Fe^{+2}
0.00	1.51	1.51	1.51	1.51	1.51	1.51
0.50	1.66	1.78	1.81	1.82	1.82	1.83
1.00	1.87	2.24	2.51	2.58	2.62	2.63
1.10	1.92	2.55	2.87	2.91	2.96	3.08
1.20	2.00	2.83	3.18	3.40	3.56	3.71
1.30	2.06	3.14	3.58	3.81	4.09	4.10
1.40	2.24	3.49	4.08	4.42	4.68	4.92
1.50	2.40	4.04	4.78	5.11	5.40	5.53
1.52	2.51	4.12	4.96	5.20	5.53	5.73
1.54	2.63	4.30	5.05	5.34	5.66	5.89
1.56	2.75	4.52	5.19	5.51	5.85	6.11
1.58	2.97	4.77	5.38	5.64	5.98	6.23
1.60	10.17	6.38	5.49	5.75	6.05	6.32
1.62	11.68	8.12	5.64	5.83	6.32	6.46
1.64	12.10	9.44	5.77	6.13	6.47	6.71
1.66	12.23	9.73	6.08	6.50	6.73	6.97
1.68	12.41	10.12	6.37	6.73	6.88	7.07
1.70	12.58	10.50	6.72	6.98	7.08	7.29
1.75	12.73	10.83	7.23	7.47	7.71	8.03
1.80	12.85	11.21	7.59	7.81	8.30	8.49
1.85	12.90	11.32	7.91	8.50	8.92	9.26
1.90	12.93	11.47	8.20	8.72	9.08	9.82

Table : D-II

3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal DY) at $30^0 \pm 0.2^0$ C.

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
2.25	-0.3723	1.9351	3.4555
2.50	-0.3525	1.8831	3.4505
2.75	-0.3723	1.8771	3.4527
3.00	-0.3220	1.8053	3.4565
3.25	-0.2432	1.6082	3.4533
3.50	-0.1848	1.4621	3.4591
3.75	-0.1401	1.3503	3.4543
4.00	-0.0886	1.2215	3.4556
4.25	-0.0467	1.1167	3.4573
4.50	0.0318	1.0795	3.4531

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
9.00	0.0413	0.8967	11.1018
9.25	0.0416	0.8959	11.1037
9.50	0.0510	0.8724	11.1000
9.75	0.0663	0.8342	11.1053
10.00	0.0768	0.8079	11.1021
10.25	0.0902	0.7745	11.1027
10.50	0.0978	0.7535	11.1079
10.75	0.1245	0.6887	11.1069
11.00	0.1721	0.5698	11.1047
11.25	0.2205	0.4488	11.1022

Table : D-III

Copper+bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one] (Chal DY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.50	0.0051	0.0638	11.3735
5.75	0.0261	0.3250	11.1474
6.00	0.0512	0.6514	10.9292
6.25	0.0676	0.8449	10.6991
6.50	0.0839	1.0486	10.4712
6.75	0.1028	1.2848	10.2481
7.00	0.1257	1.5709	10.0332
7.25	0.1412	1.7645	9.8086
7.50	0.1590	1.9867	9.5898

Table : D-IV

Nickel+bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal DY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.75	0.0124	0.1550	11.1318
6.00	0.0326	0.4049	10.9051
6.25	0.0421	0.5261	10.6668
6.50	0.0600	0.7498	10.4168
6.75	0.0795	0.9935	10.2151
7.00	0.1040	1.2996	9.9999
7.25	0.1209	1.5107	9.7756
7.50	0.1382	1.7268	9.5536
7.75	0.1550	1.9367	9.3326

Table : D-V

Cobalt+bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal DY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
6.00	0.0100	0.1249	10.8791
6.25	0.0192	0.2399	10.6391
6.50	0.0385	0.4811	10.4124
6.75	0.0590	0.7373	10.1880
7.00	0.0806	1.0072	9.9667
7.25	0.1010	1.2621	9.7455
7.50	0.1229	1.5356	9.5288
7.75	0.1370	1.7118	9.3016
8.00	0.1487	1.8580	9.0715

Table : D-VI

Ironr+bis[3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal DY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
6.25	0.0018	0.0224	10.6200
6.50	0.0181	0.2262	10.3884
6.75	0.0390	0.4874	10.1628
7.00	0.0599	0.7485	9.9392
7.25	0.0830	1.0371	9.7200
7.50	0.1001	1.2507	9.4942
7.75	0.1160	1.4494	9.2681
8.00	0.1301	1.6254	9.0403
8.25	0.1538	1.9215	8.8308

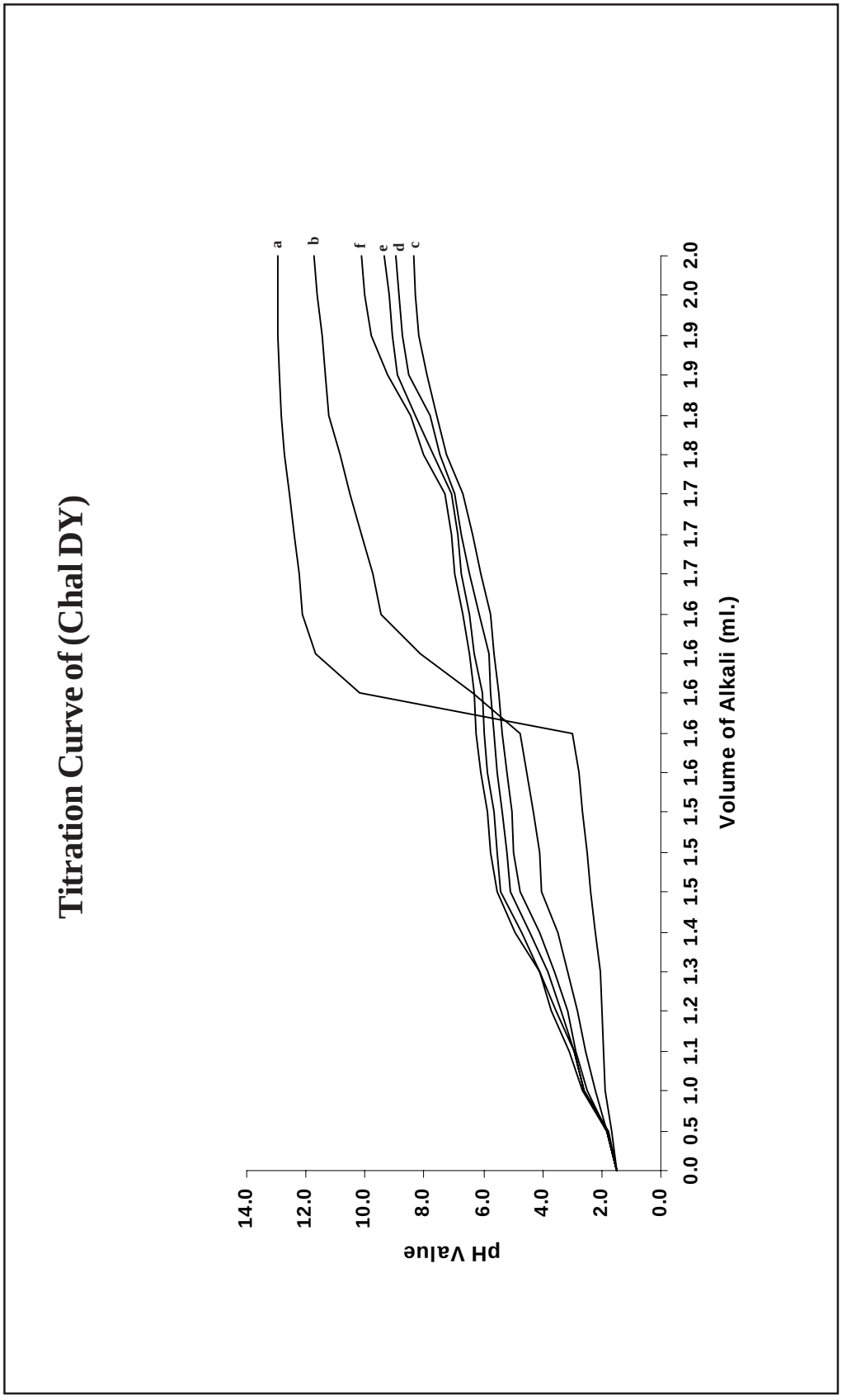

Titration Curve of (Chal DY)
pH Value
Volume of Alkali (ml.)
a
b
f
e
d
c
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0.0 0.5 1.0 1.1 1.2 1.3 1.4 1.5 1.5 1.5 1.6 1.6 1.6 1.6 1.6 1.7 1.7 1.7 1.8 1.8 1.9 1.9 2.0 2.0

Fig. : D-I

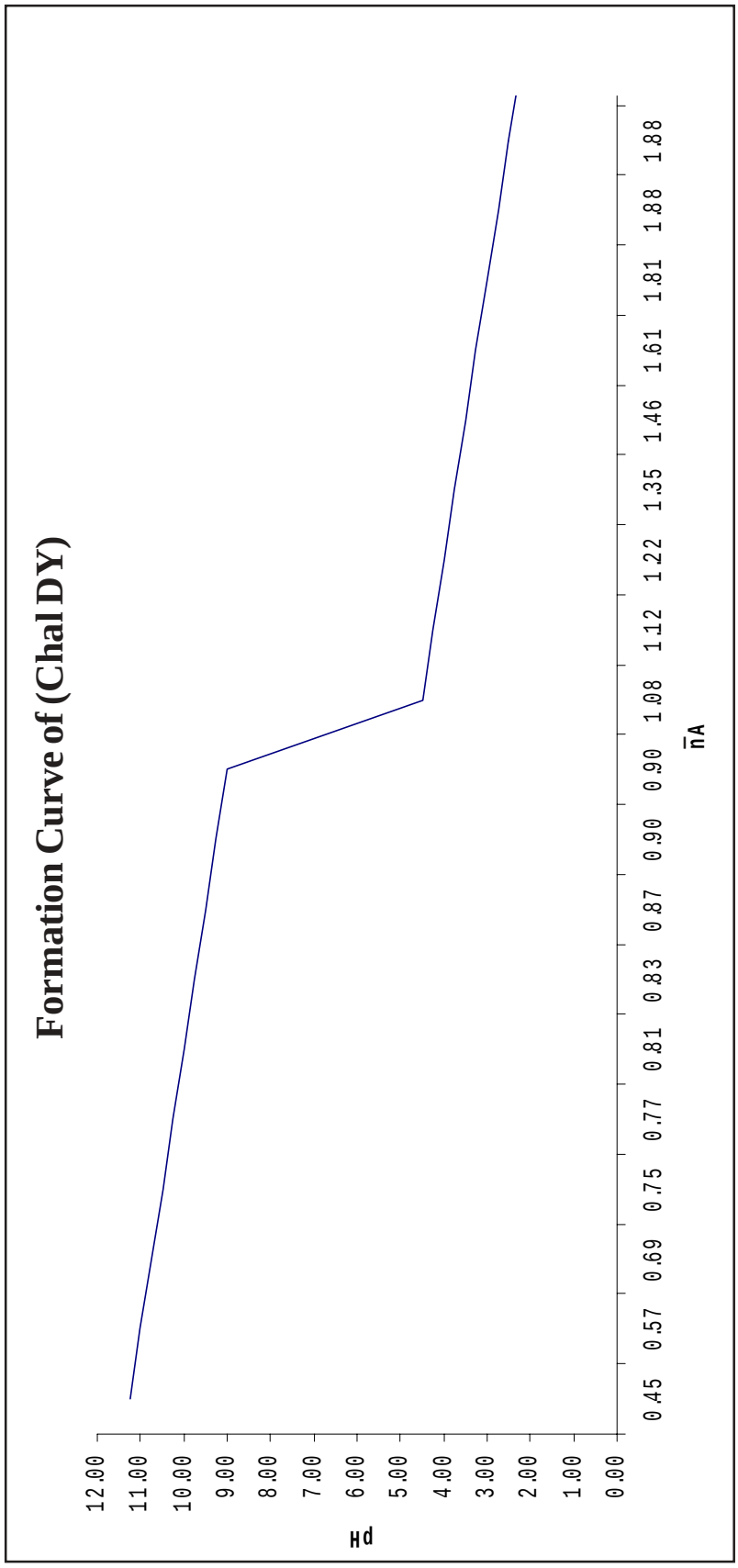

Formation Curve of (Chal DY)
pH
12.00
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.45 0.57 0.69 0.75 0.77 0.81 0.83 0.87 0.90 0.90 1.08 1.12 1.22 1.35 1.46 1.61 1.81 1.88 1.88
n̄A

Fig.- D-2

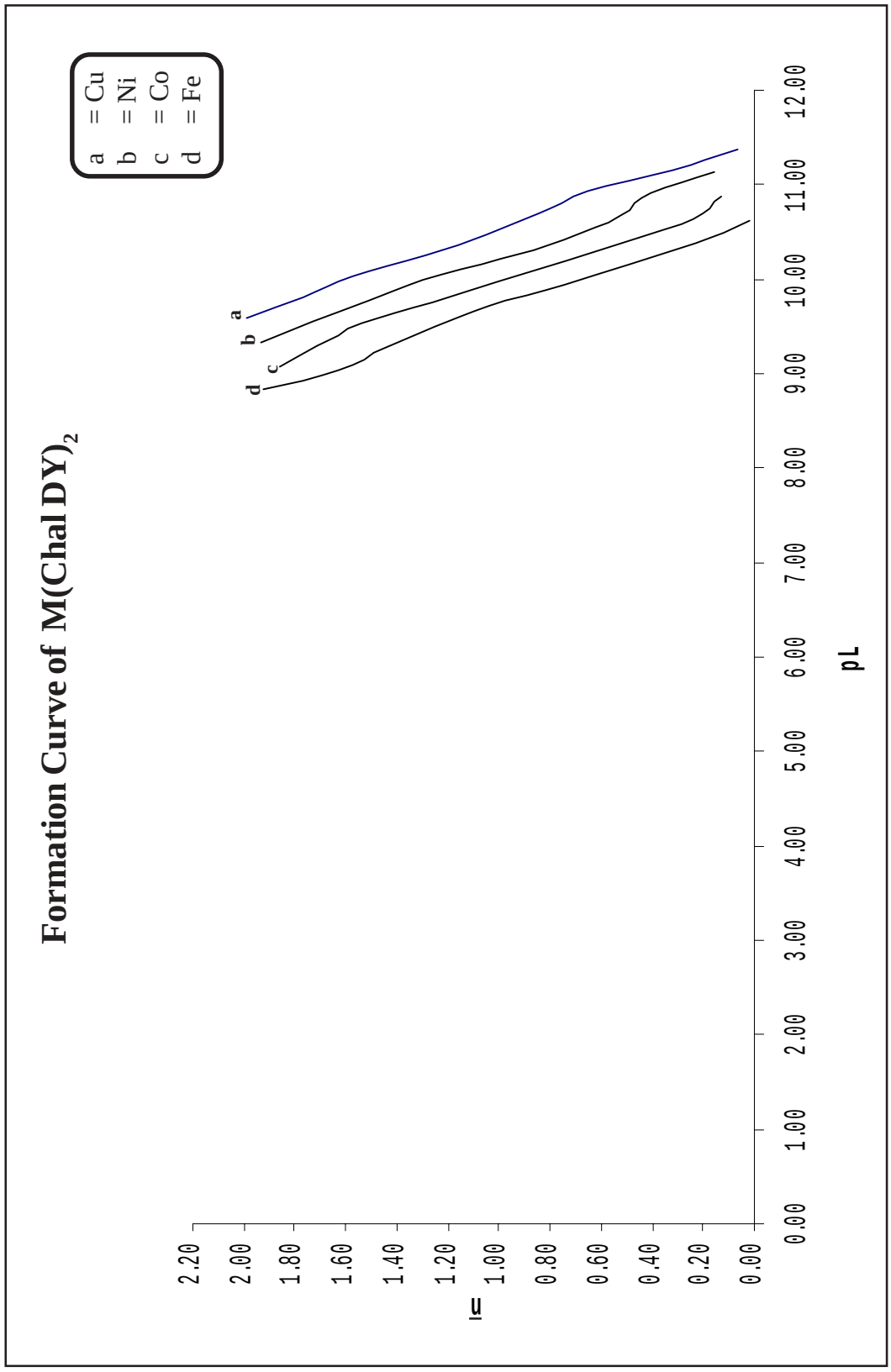

Formation Curve of M(Chal DY)2
a = Cu
b = Ni
c = Co
d = Fe
a
b
c
d
n̄
pL
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
2.20
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00

Fig.- D-3

Fig.- D-4
Linear Plot of Ligand (Chal DY)
Chal DY at $30^0 \pm 0.2^0$ C

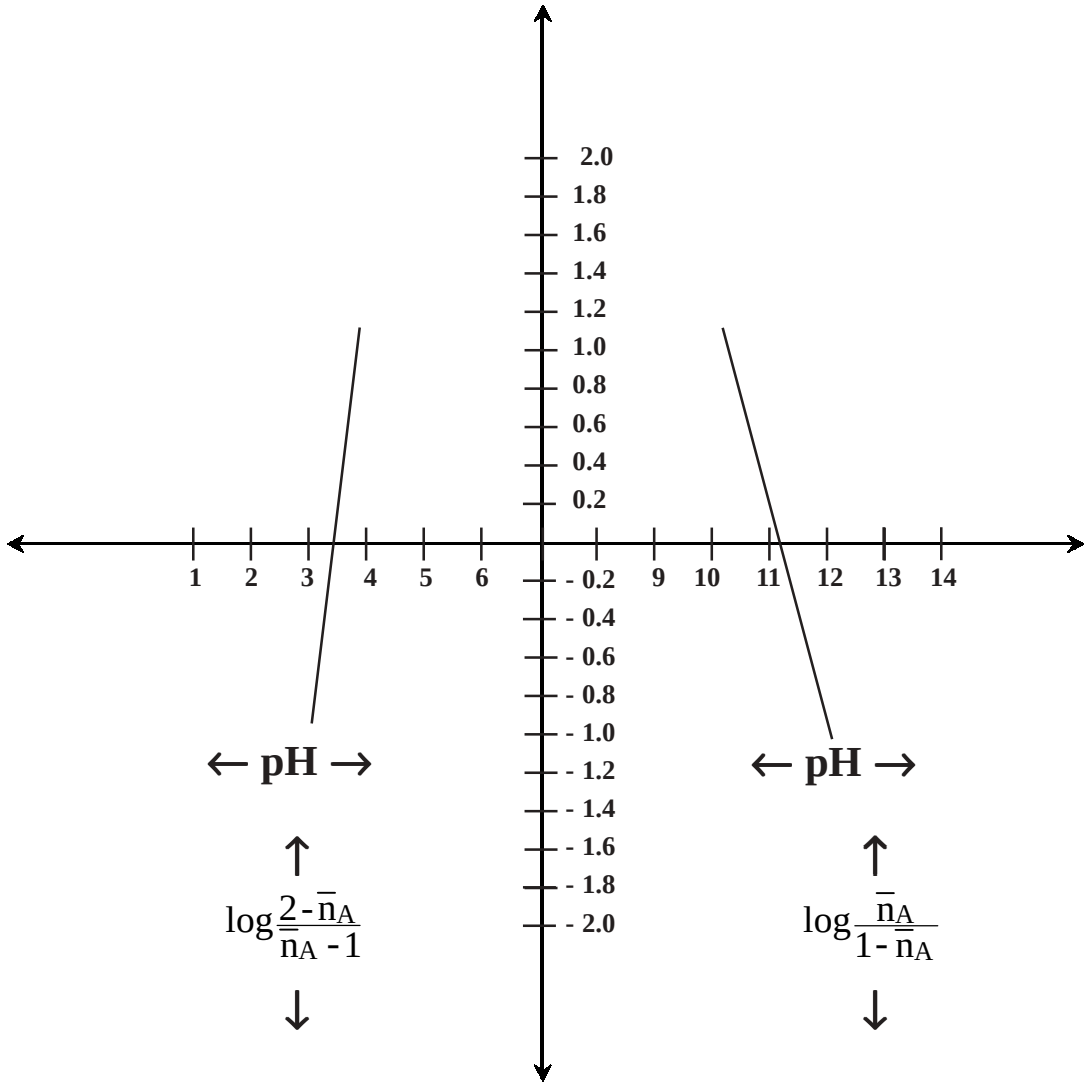


Fig.- D-5
Linear Plot of $M(Chal\,DY)_2$

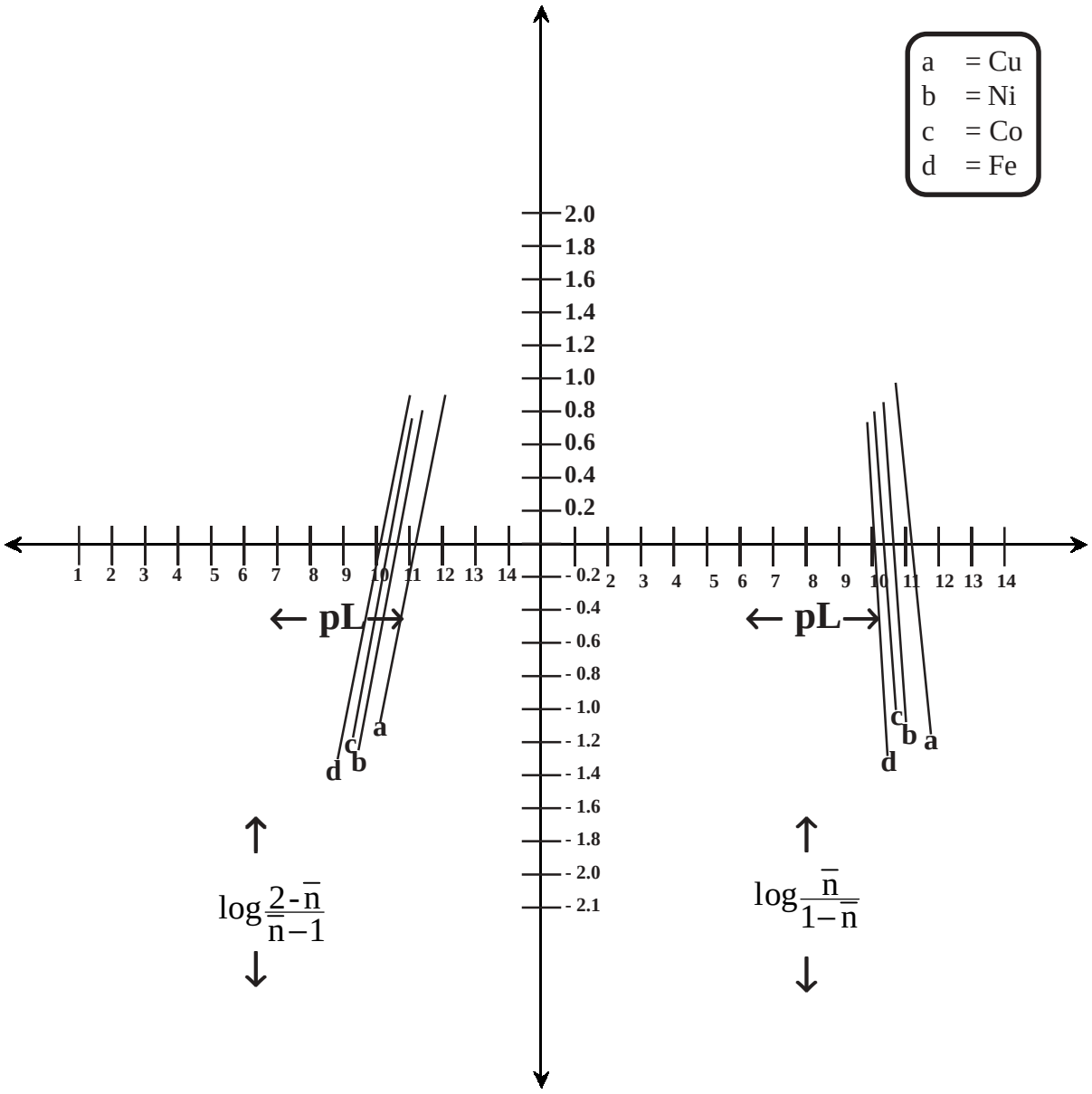


Table : E-I
The pH titration reading of acid, acid + ligand (Chal EY) and acid + ligand (Chal EY) + metal ion.

N^0 = 0.5M, E^0 = 0.02M. V^0 = 40.0ml

T^0_L = 5 x 10-3M T^0_M = 1 x 10-3M t = $30^0 \pm 0.2^0$C,

u^0 = 0.1M.

Solvent = Dioxane : Water :: 60 : 40 (v/v)

Vol. of Alkali added.	Acid	Acid + ligand.	pH meter reading (B)			
			Acide + ligand (Chal EY) + metal ion:			
			Cu^{+2}	Ni^{+2}	Co^{+2}	Fe^{+2}
0.00	1.51	1.51	1.51	1.51	1.51	1.51
0.50	1.66	1.80	1.83	1.84	1.84	1.85
1.00	1.87	2.21	2.73	3.78	2.81	2.86
1.10	1.92	2.40	3.02	3.07	3.11	3.16
1.20	2.00	2.75	3.38	3.45	3.51	3.58
1.30	2.06	3.28	3.79	3.84	3.90	3.94
1.40	2.24	4.32	4.41	4.44	4.51	4.58
1.50	2.40	5.24	5.12	5.17	5.22	5.28
1.52	2.51	5.48	5.24	5.30	5.35	5.42
1.54	2.63	5.73	5.39	5.48	5.52	5.60
1.56	2.75	5.98	5.50	5.59	5.68	5.77
1.58	2.97	6.30	5.61	5.76	5.81	6.00
1.60	10.17	6.98	5.76	5.83	5.93	6.23
1.62	11.68	8.03	5.82	5.93	6.11	6.52
1.64	12.10	8.33	5.93	6.02	6.34	6.73
1.66	12.23	9.00	6.04	6.11	6.51	7.00
1.68	12.41	9.48	6.12	6.32	6.72	7.26
1.70	12.58	9.72	6.30	6.51	6.57	7.42
1.75	12.73	10.25	6.76	7.00	7.30	8.02
1.80	12.85	10.51	7.12	7.29	7.74	8.43
1.85	12.90	10.66	7.31	7.43	7.85	8.52
1.90	12.93	10.82	7.41	7.53	8.00	8.60
1.95	12.95	10.93	7.52	7.60	8.14	8.66
2.00	12.97	11.25	7.55	4.62	8.17	8.70

Table : E-II

3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal EY) at $30^0 \pm 0.2^0$ C.

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
2.25	0.3902	1.9801	3.7681
2.50	0.3731	1.9347	3.7607
2.75	0.3567	1.8923	3.7632
3.00	-0.3303	1.8261	3.7623
3.25	-0.2742	1.6857	3.7655
3.50	-0.2266	1.5667	3.7693
3.75	-0.1976	1.4940	3.7603
4.00	-0.1679	1.4198	3.7629
4.25	-0.1480	1.3700	3.7645
4.50	-0.1265	1.3163	3.7611
4.75	-0.1106	1.2765	3.7686
5.00	-0.0918	1.1229	3.7649

B	V_2-V_1	$\bar{n}A$	$\log^P K_2^H$
9.00	0.0350	0.9125	11.0061
9.25	0.0496	0.8759	11.0078
9.50	0.0524	0.8689	11.0092
9.75	0.0668	0.8329	11.0063
10.00	0.0826	0.7934	11.0042
10.25	0.1029	0.7427	11.0002
10.50	0.1203	0.6992	11.0048
10.75	0.1583	0.6042	11.0088
11.00	0.2134	0.4665	11.0013
11.25	0.2719	0.3204	11.0067

Table : E-III

Copper+bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal EY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
4.75	0.0020	0.0250	12.3287
5.00	0.0098	0.1228	12.0876
5.25	0.0242	0.3032	11.8544
5.50	0.0469	0.5873	11.6319
5.75	0.0663	0.8299	11.4069
6.00	0.0877	1.0972	11.1861
6.25	0.1096	1.3707	10.9701
6.50	0.1372	1.7154	10.7618
6.75	0.1600	2.0003	10.5518

Table : E-IV

Nickel+bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal EY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
5.00	0.0061	0.0765	12.0838
5.25	0.0117	0.1465	11.8400
5.50	0.0210	0.2630	11.6009
5.75	0.0415	0.5194	11.3755
6.00	0.0635	0.7943	11.1535
6.25	0.0900	1.1280	10.9395
6.50	0.1119	1.4879	10.7325
6.75	0.1380	1.7252	10.5132
7.00	0.1489	1.8610	10.2820

Table : E-V

Cobalt+bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal EY) at $30^0 \pm 0.2^0$ C.

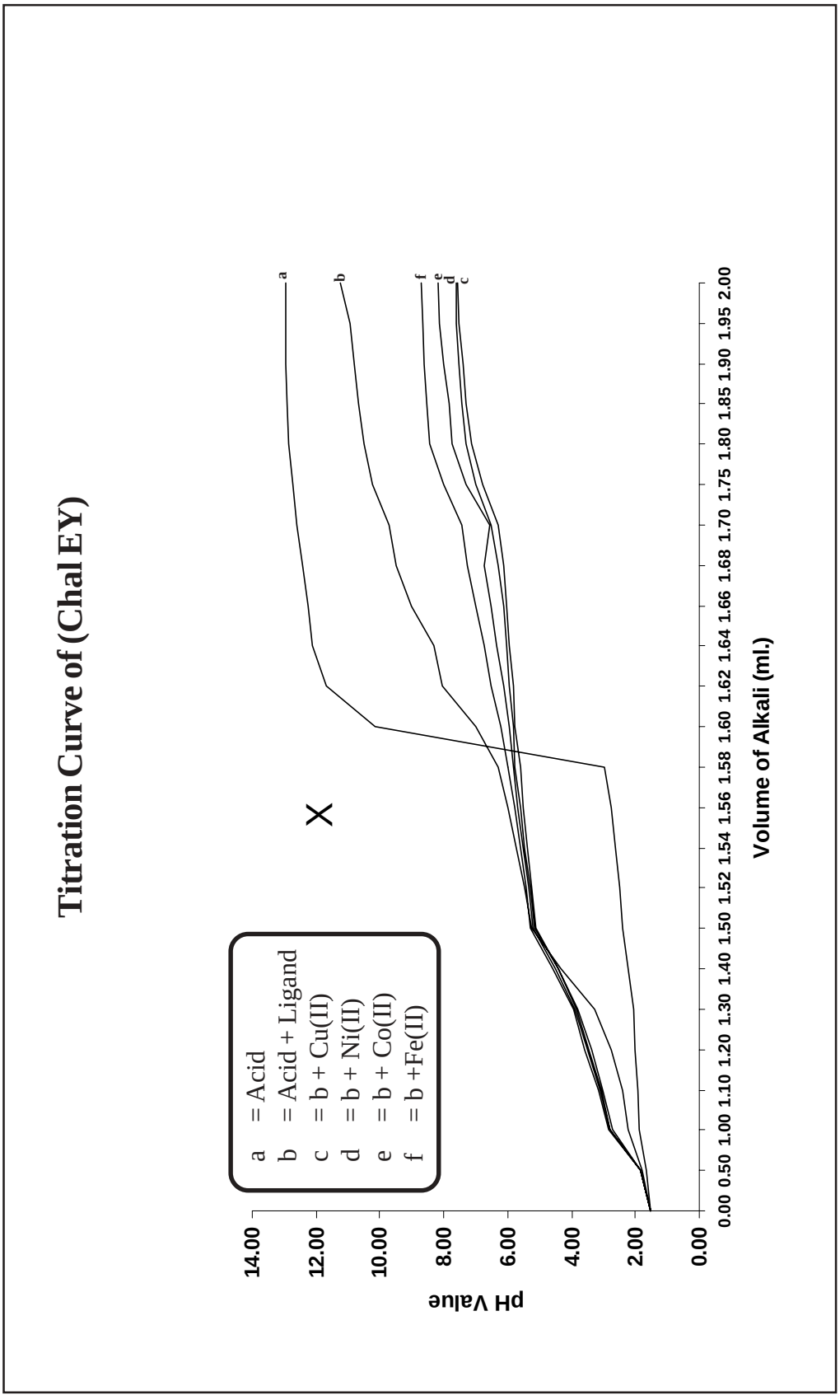
B	V_3-V_2	$\bar{n}$	$_pL$
5.50	0.0160	0.2003	11.5951
5.75	0.0248	0.1465	11.3555
6.00	0.0361	0.4540	11.1194
6.25	0.0485	0.6065	10.8845
6.50	0.0660	0.8252	10.6569
6.75	0.0874	1.0926	10.4359
7.00	0.1076	1.3448	10.2152
7.25	0.1275	1.5933	9.9961
7.50	0.1563	1.9530	9.7949

Table : E-VI

Iron+bis[3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one](Chal EY) at $30^0 \pm 0.2^0$ C.

B	V_3-V_2	$\bar{n}$	$_pL$
6.25	0.0175	0.2188	10.8474
6.50	0.0283	0.3538	10.6101
6.75	0.0422	0.5275	10.3768
7.00	0.0579	0.7236	10.1466
7.25	0.0726	0.9072	9.9158
7.50	0.0902	1.1270	9.6900
7.75	0.1117	1.3956	9.4715
8.00	0.1322	0.1117	9.2351
8.25	0.1541	1.9250	9.0221

Fig. : E-1


Titration Curve of (Chal EY)
a = Acid
b = Acid + Ligand
c = b + Cu(II)
d = b + Ni(II)
e = b + Co(II)
f = b +Fe(II)
pH Value
Volume of Alkali (ml.)
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.00 0.50 1.00 1.10 1.20 1.30 1.40 1.50 1.52 1.54 1.56 1.58 1.60 1.62 1.64 1.66 1.68 1.70 1.75 1.80 1.85 1.90 1.95 2.00

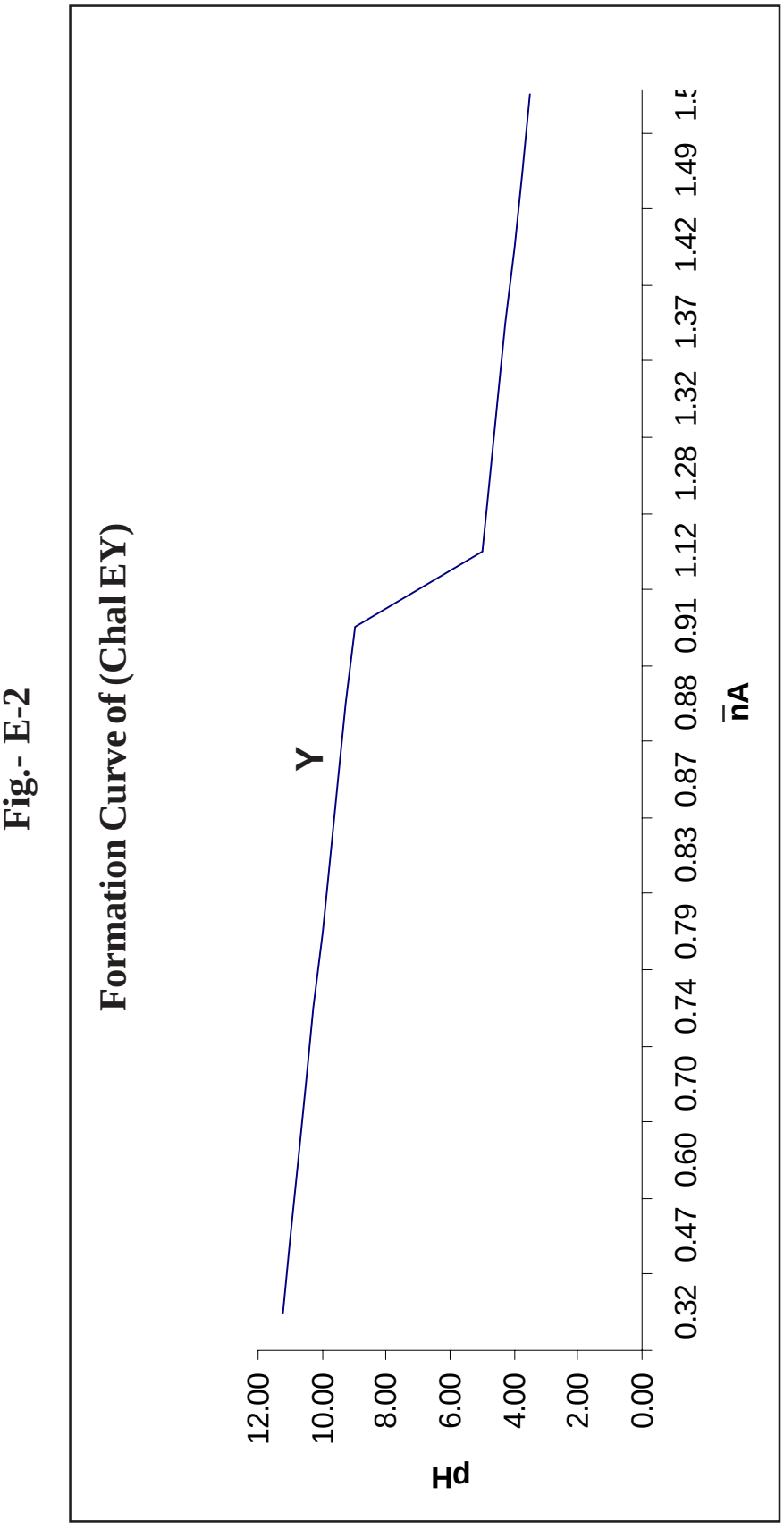

Formation Curve of (Chal EY)
Y
pH
12.00
10.00
8.00
6.00
4.00
2.00
0.00
0.32 0.47 0.60 0.70 0.74 0.79 0.83 0.87 0.88 0.91 1.12 1.28 1.32 1.37 1.42 1.49
n̄A

Fig.- E-2

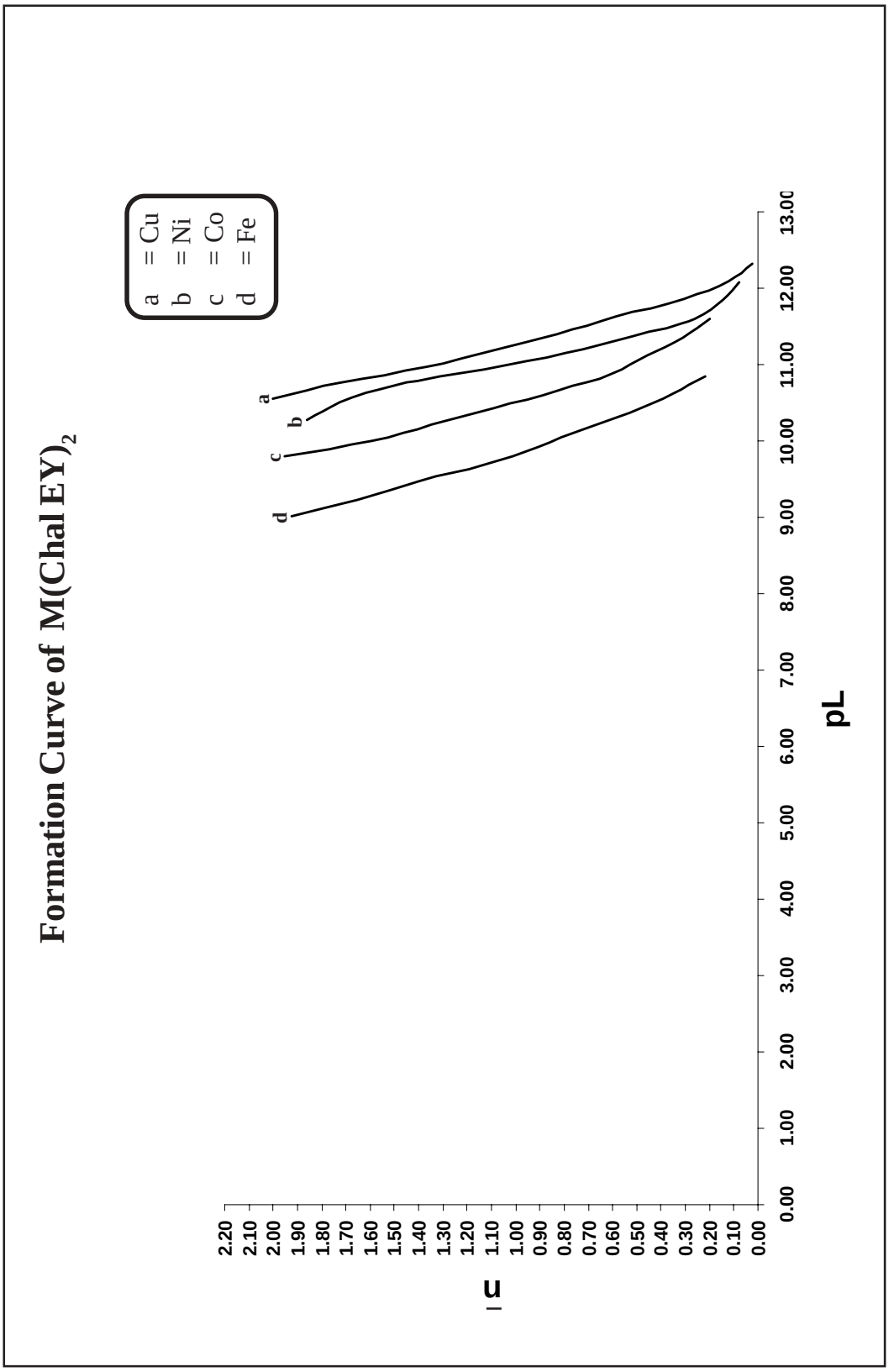

Formation Curve of M(Chal EY)2
a = Cu
b = Ni
c = Co
d = Fe
a
b
c
d
n̄
pL
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
1.20
1.30
1.40
1.50
1.60
1.70
1.80
1.90
2.00
2.10
2.20
0.00
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00

Fig.- E -3

Fig.- E-4
Linear Plot of Ligand Chal EY
Chal EY at $30^0 \pm 0.2^0$ C

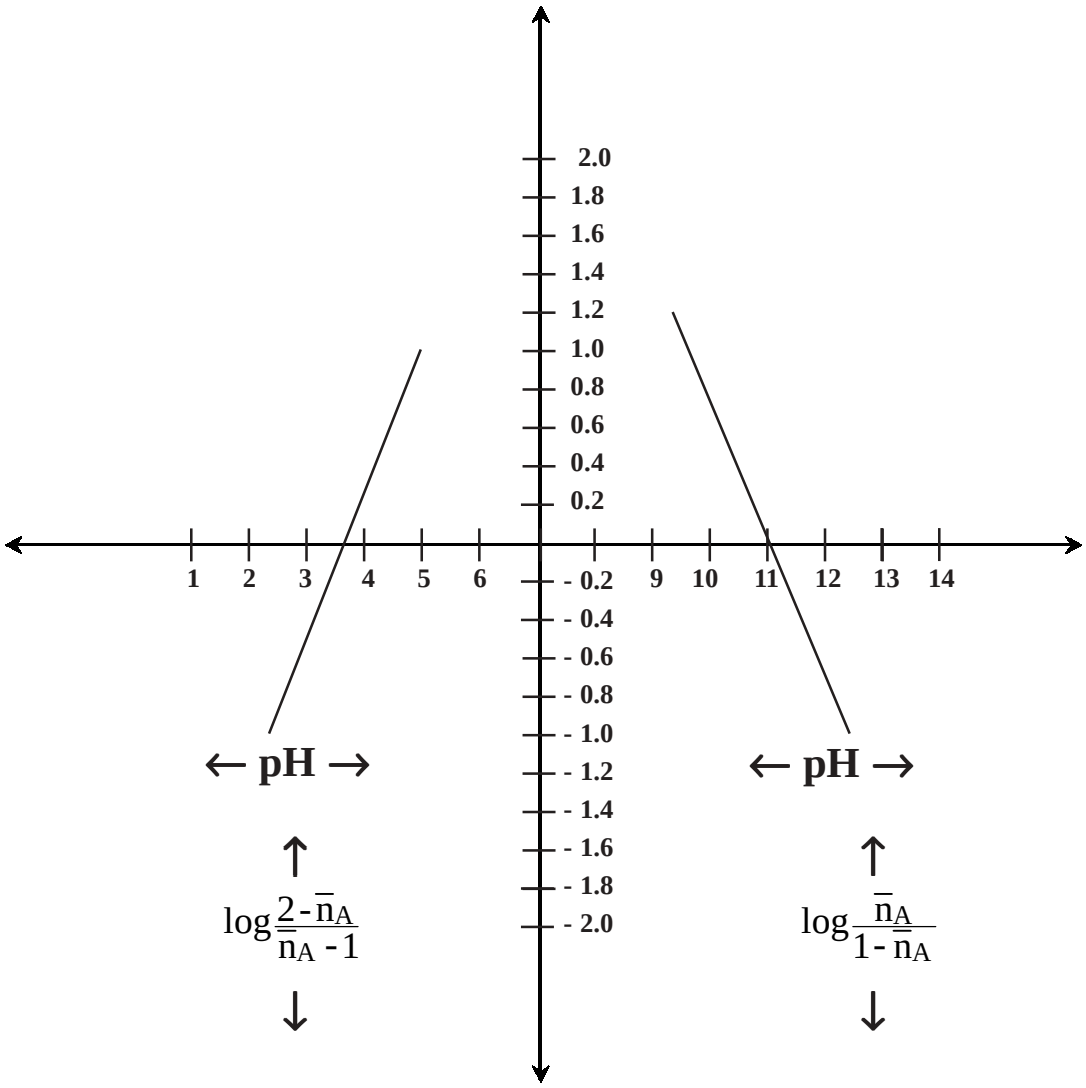
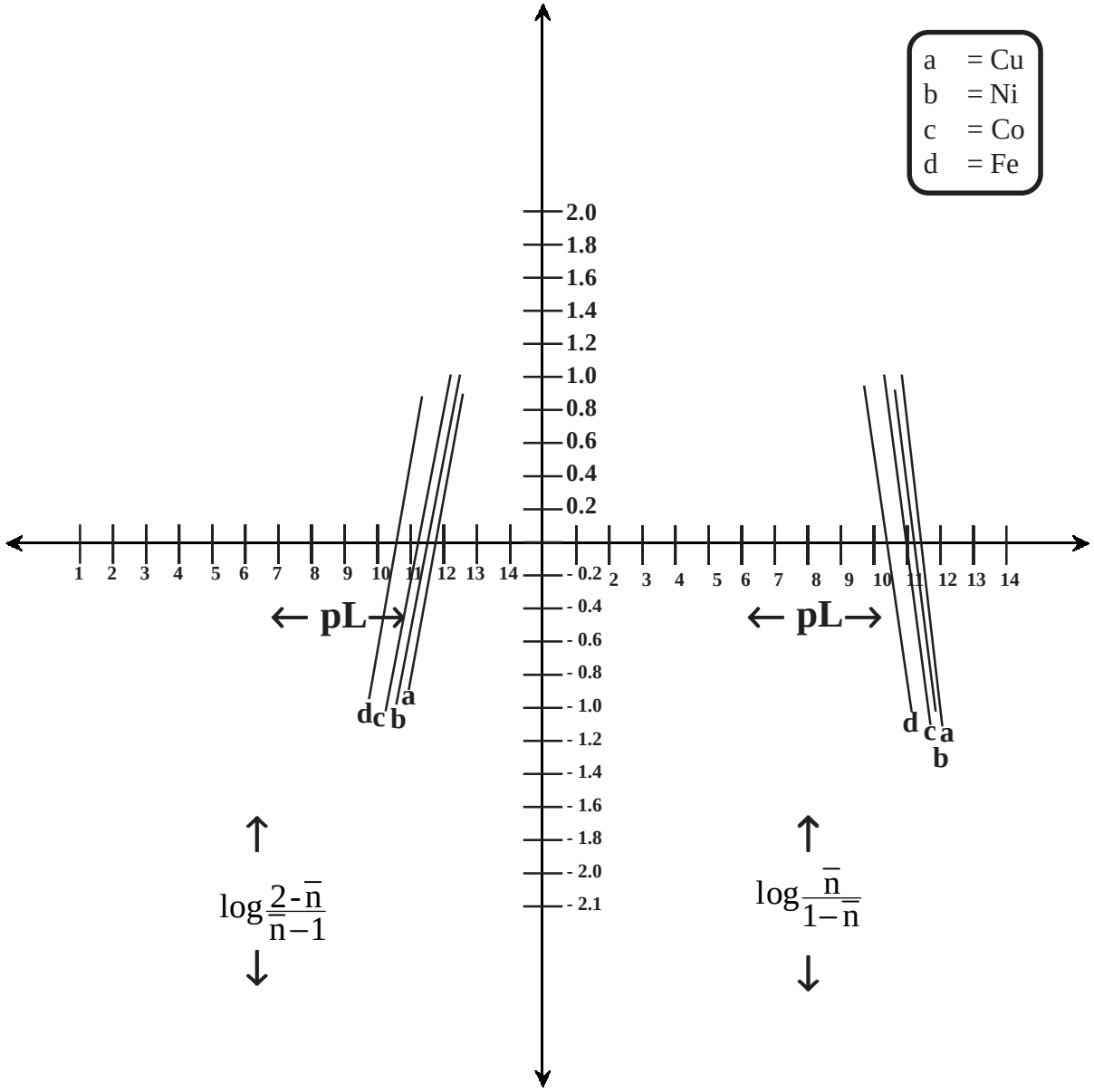


Fig.- E-5
Linear Plot of $M(Chal\,EY)_2$



GENERAL DISCUSSION

GENERAL DISCUSSION

LIGANDS:

The large number of 4-hydroxycoumarin derivatives forming metal complexes. We have synthesized four new 4-hydroxycoumarin derivatives like

(1) 3-[{3-(2'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-AX)

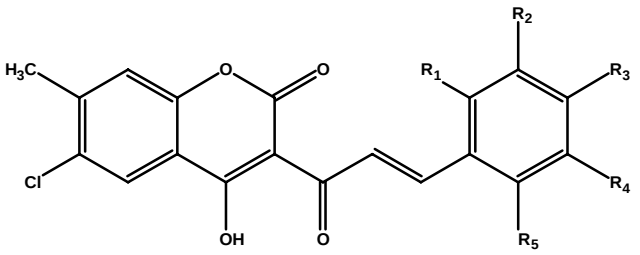
(2) 3-[{3-(4'-chlorophenyl)}-prop-2-enoyl]-4-hydroxy-6-chloro-7-methyl-2H-chromen-2-one (Chal-BX)

(3) 3-[{3-(2'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-DY)

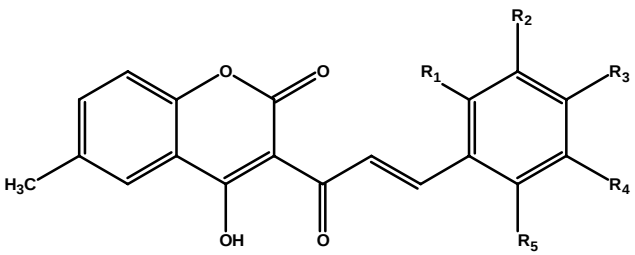
(4) 3-[{3-(4'-chloro) phenyl}-prop-2-enoyl]-4-hydroxy-6-methyl-2H-chromen-2-one (Chal-EY)

They are different in colours; dissolve in almost all organic solvents. Their characteristic properties are discussed in part-I, chapter-I. These ligands have reactive system containing hydroxyl group (-OH) and carbonyl group (C=O). So situated as to form heterocyclic ring with metal ions. Thus, they are good chelating agents or ligands we have synthesized metal complexes of Cu(II), Ni(II), Co(II) and Fe(II) with these ligands.

On the basis of synthesis elemental analysis and spectral studies. The general structure of the ligands proposed to represented as...



[X]



[Y]

Where

R_1,R_2, R_3 & R_4 are as under....

Chal AX	X-1	(i) R_2, R_3, R_4, R_5 - H (ii) R_1 - Cl	Chal DY	X-2	(i) R_2, R_3, R_4, R_5 - H (ii) R_1 - Cl
Chal BX	Y-1	(i) R_1, R_2, R_4, R_5 - H (ii) R_3 - Cl	Chal EY	Y-2	(i) R_1, R_2, R_4, R_5 - H (ii) R_3 - Cl

The elemental analysis as prescribed in Chapter-1 Table-1 agrees with theoretically expected value. Thus, supporting the suggested molecular camphor method.

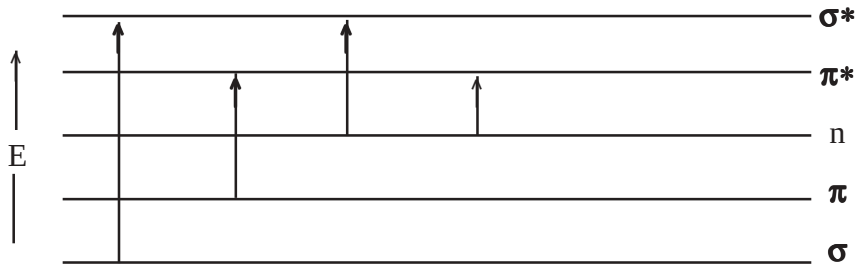
Absorption spectral studies of ligands. (UV & VIS):

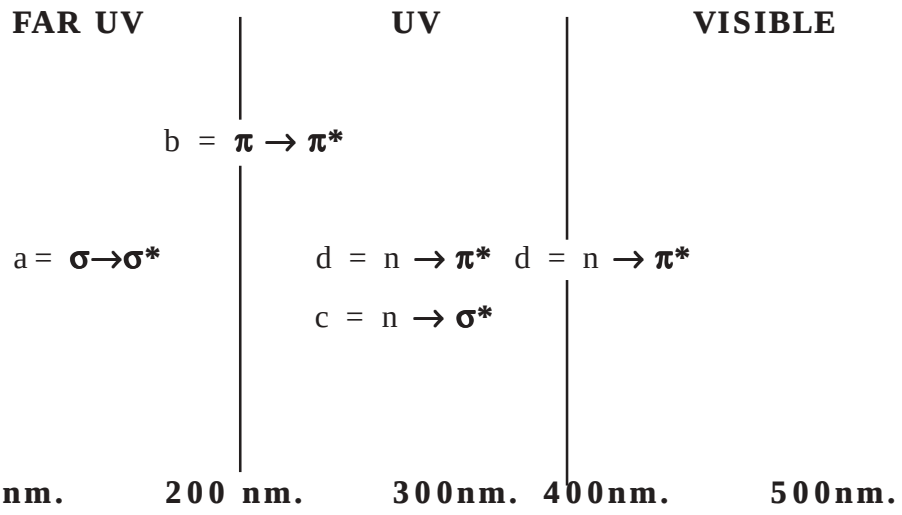
The absorption spectra of the ligands in UV & visible regions show three bands at 250 - 348 nm, 275 - 364 nm and 349 - 399 nm. These are attributed to **$\pi \rightarrow \pi^*$** and **$n \rightarrow \pi^*$** transactions.

In general as it is known that the absorption of light energy by organic compound in visible and ultraviolet region involves transition of electrons from the ground state to higher states. The electronic transitions that are involved in the ultraviolet and visible regions are of the following types.

$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$

Diagrammatically they are represented as under,

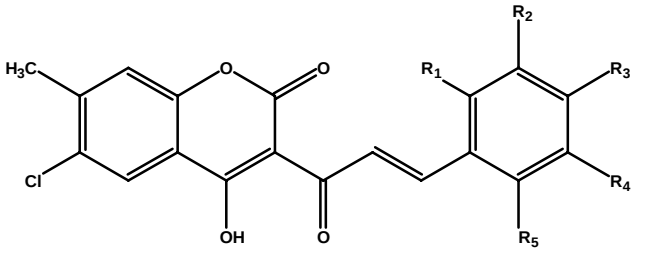




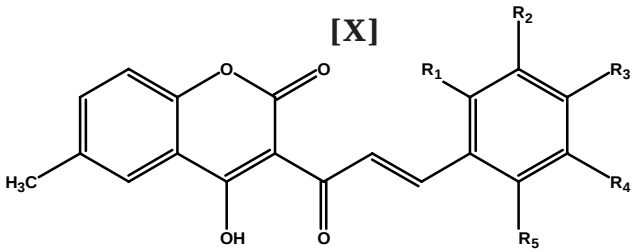
σ - electrons are most bounded to the nuclei and hence requied considerable high energy for excitation while, **π** and n electron require less energy. Accordingly the energy require for **σ→σ*** transition is very high and compounds such as saturated hydrocarbons show absorption in the vaccum ultraviolet region.

Transition to antibonding **π*** orbitals i.e. n**→π*** and **π→π*** associated with unsaturated centres in the molecule occur at longer wavelength. n**→σ*** transactions are of intermediate energy between n**→σ*** and n**→π*** transactions.

The absorption maxima, λmax in nm and corresponding (log ε) value of lingands are presented here.



[X]



[Y]

Where,

R_1, R_2, R_3, R_4 & R_5 are mentioned on page no. 33, 34 (Chapter - 1)

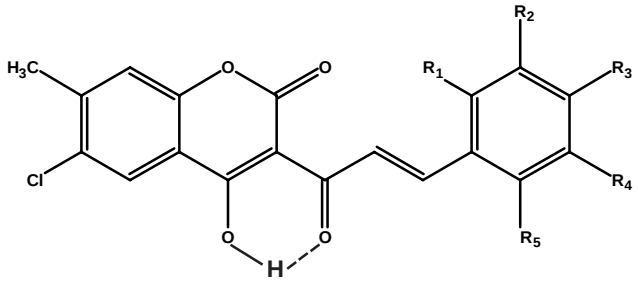
Absorption maximum(λ max) and log ε of ligands

SR. NO.	LIGANDS	λ max. (nm)	log ε
1	Chal AX	339.2	3.198
		314.0	3.748
		293.6	3.788
		279.2	3.749
2	Chal BX	350.0	2.807
		308.0	3.469
		293.6	3.538
		280.4	3.505
3	Chal DY	348.2	1.098
		333.3	1.353
		364.5	1.651
4	Chal EY	333.1	1.930
		400.8	1.443
		250.7	0.042

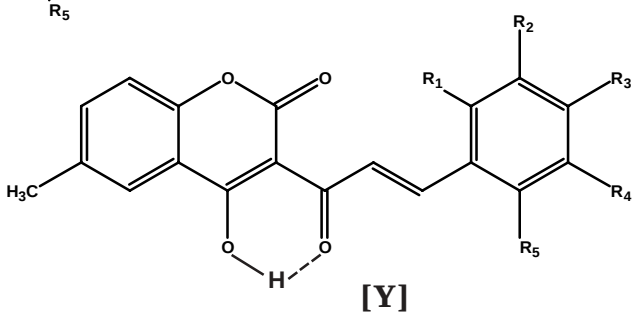
It is found that position of λmax for all of the ligands is almost the same. The observations indicate that the substitution in the 4-hydroxycoumarin attached to acetyl group does not cause much variation in the position of λmax. The slight shift in the λmax due to change in molecular weight of the ligands.

IR Spectral studies of ligands :

The IR Spectra of all the ligands (page 56 to 59) are identical with slight variation in group frequency as shown in table below, which are according to the suggested structure of the all ligands molecules.



[X]



[Y]

Where,

R_1, R_2, R_3, R_4 & R_5 are under.

Ligand	Substitutions				
	R_1	R_2	R_3	R_4	R_5
Chal AX	Cl	H	H	H	H
Chal BX	H	H	Cl	H	H
Chal DY	Cl	H	H	H	H
Chal EY	H	H	Cl	H	H

NMR Spectral studies of ligands:

The NMR spectral bands are presented on page 52 to 55and their positions are presented in Table IIIA to IIIE on page 38 to 41. The structure of the ligand molecule is further supported by the NMR spectral data.

MASS spcectral studies of ligands :

For the purpose of supporting the proposed structure of the ligand. The mass spectral analysis was carried out. The results are presented on page 60 to 63 and corresponding fragmentation is shown on page 46 to 49. These data are also in good agreement with proposed structure of ligand molecule.

Metal Complexes:

Metal Complexes of Cu(II), Ni(II), Co(II) and Fe(II) were synthesized and the studies of their characteristic, properties are mentioned in Part-1, Chapter-II to V.

IR frequancy of the ligand molecules.

LIGAND	Hydroxy -OH		Alkane -CH_3				-CH		Aromatic			Ketone
	O - H *str.*	-OH *band.*	C - H *str. (asym)*	C - H *str. (sym)*	C - H *def. (asym)*	C - H *def. (sym)*	C - H *str.*	C - H *band.*	C = C *str.*	C - H i.p *def.*	C - H o.o.p. *def.*	C =O *str.*
Chal AX	3398	1319	2923	2854	1438	1382	3066	1292	1577	1213	860	1710 1670
Chal BX	3425	1382	2925	2854	1434	1382	3055	1203	1529	1290	866	1726 1682
Chal DY	3406	1242	3081	2923	1438	1389	3083	1242	1575	1099	832	1703 1687
Chal EY	3375	1310	2923	2852	1453	1385	3026	1261	1525	1234	827	1701 1680

Copper Complexes :

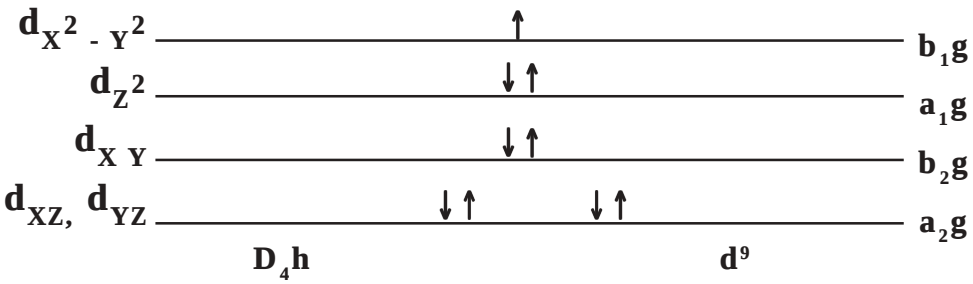
All the copper complexes are insoluble in water and slightly soluble in alcohol and other organic solvents. From the elemental analysis it is found that the copper complexes are the type ML_2.

The molecular weight determination by Rass camphor method although not very reliable still it is in agreement with the suggested molecular formula of copper complexes.

The conductivity of the solution of copper complexes in DMF was measured and low values of conductivity observed suggests that the metal complexes are non-ionic in nature.

In the absorption spectra of complexes, the absorption maxima, which are due to the ligand part, are very strong. The absorption bands characteristic of metal ion alone are usually relatively weak. They are called Laporte forbidden transition. These transition which corresponds to the electron shift in the unfilled 'd' orgitals of the transition metal may be observed in a free metal ions as well as in a metal complexes. Although they are frequently intensified by co-ordination of the metal ion. Calvin and co-workers[22] observed absorption bands in the visioble region due to the forbidden transition and also the k type of bands characteristic of the ligands in the ultraviolet region. In the case of Cu(II), ethyl acetoacetate and other substituted B-diketonic complexes the intensity of the absorption characterstic of Cu^{+2} ion is much weaker than that of 'K' type of bonds Calvin co-workers[22] concluded from the experimental data that the influence of a metal ion on the characteristic absorption is much weaker than the ligand which has a large conjugated system. Makenzie and co-worker[23] relate the magnetic properties with the absorption spectra of paramagnetic chelates have absorption and similar to the chelating agents. In the present case the absorption spectra of copper complexes show all the three characteristic bonds of the ligand system and two bonds due to d-d transition of the metal ion. The position of the ligand bands are shifted which may be due to the interaction of the ligand with metal ion.

The tetragonal crystal field diagram Cu^{+2} is under.[24,25]



Thus, three spin allowed transition are expected. All are d-d transition and hence would the Laporte forbidden. They are therefore expected to be weak. The spectrum shows two bonds, which are assigned as follows.

nm	**transition**
300 - 370	$2A_1g \leftarrow 2B_1g$
818 - 900	$2B_2g \leftarrow 2B_1g$

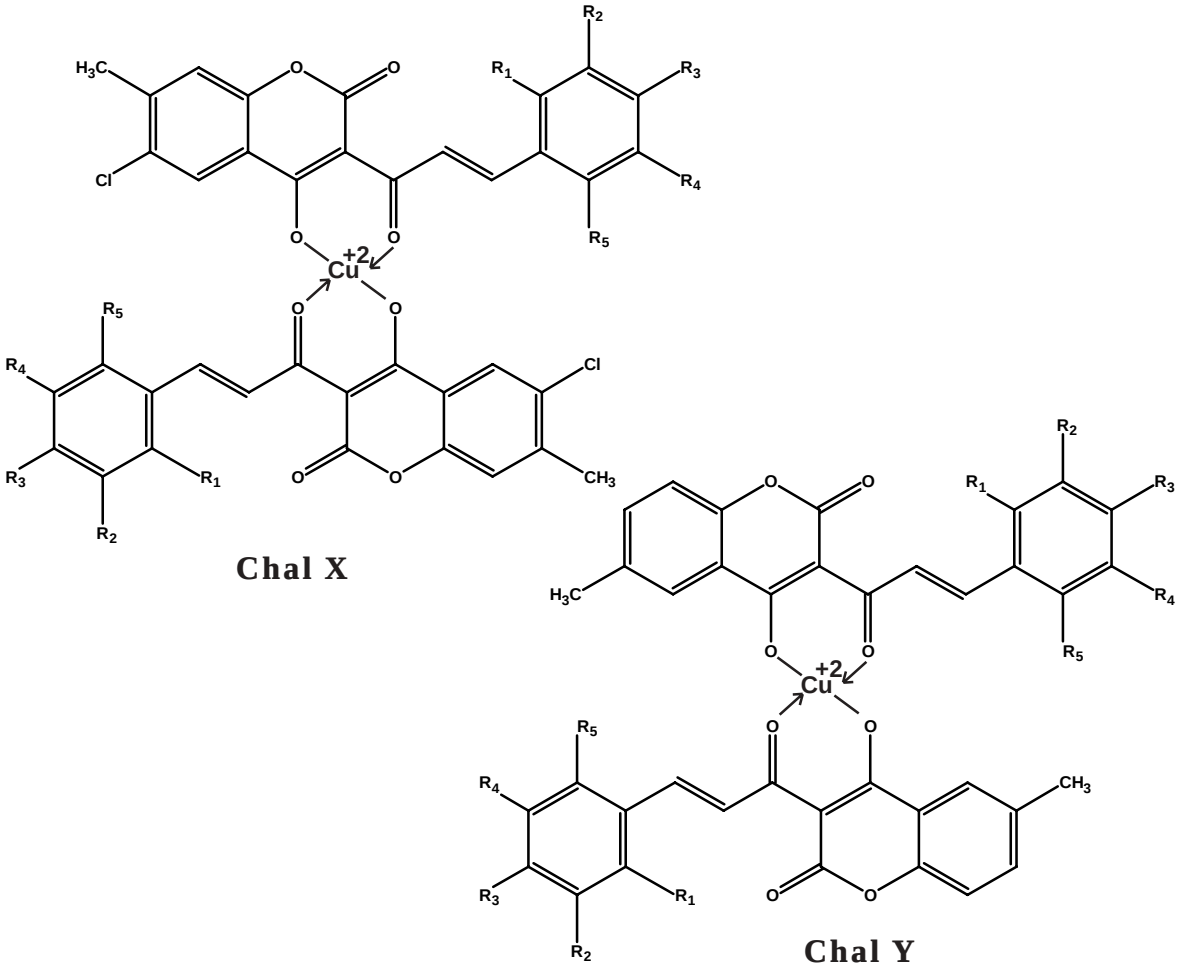
The band corresponding to $2Eg \leftarrow 2B_1g$ transititon would have overlaped with the strong charge transfer band of the spectra. Thus, indicated D_4h symmetry of the copper complex.

Magnetic properties:

The magnetic moment of all the copper complexes are in the range 1.93 - 2.08 B.M. These values are greater than the spin only value for one unpaired electron (1.73 B.M.). The access value is considered to be due to spin orbital coupling.[26,27]

ESR Spectra :

The ESR spectra (page 86 to 89) of copper complexes are discussed in chapter-2 page reveals that copper complexes are tetragonal with unpaired electron in the $d_{x^2-y^2}$ optical therefore there is no Cu-Cu interaction. The $g \parallel > g \perp$ support D_4h symmetry of the copper complexes.



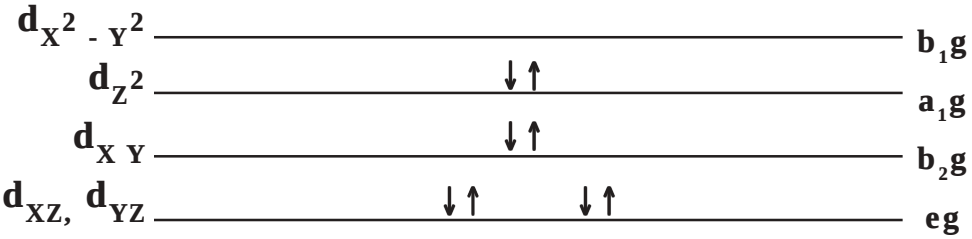
Where R_1, R_2, R_3, R_4 & R_5 are as under:

Complexes	Substitutions				
	R_1	R_2	R_3	R_4	R_5
M(Chal $AX)_2$-Z	Cl	H	H	H	H
M(Chal $BX)_2$-Z	H	H	Cl	H	H
M(Chal $DY)_2$-Z	Cl	H	H	H	H
M(Chal $EY)_2$-Z	H	H	Cl	H	H

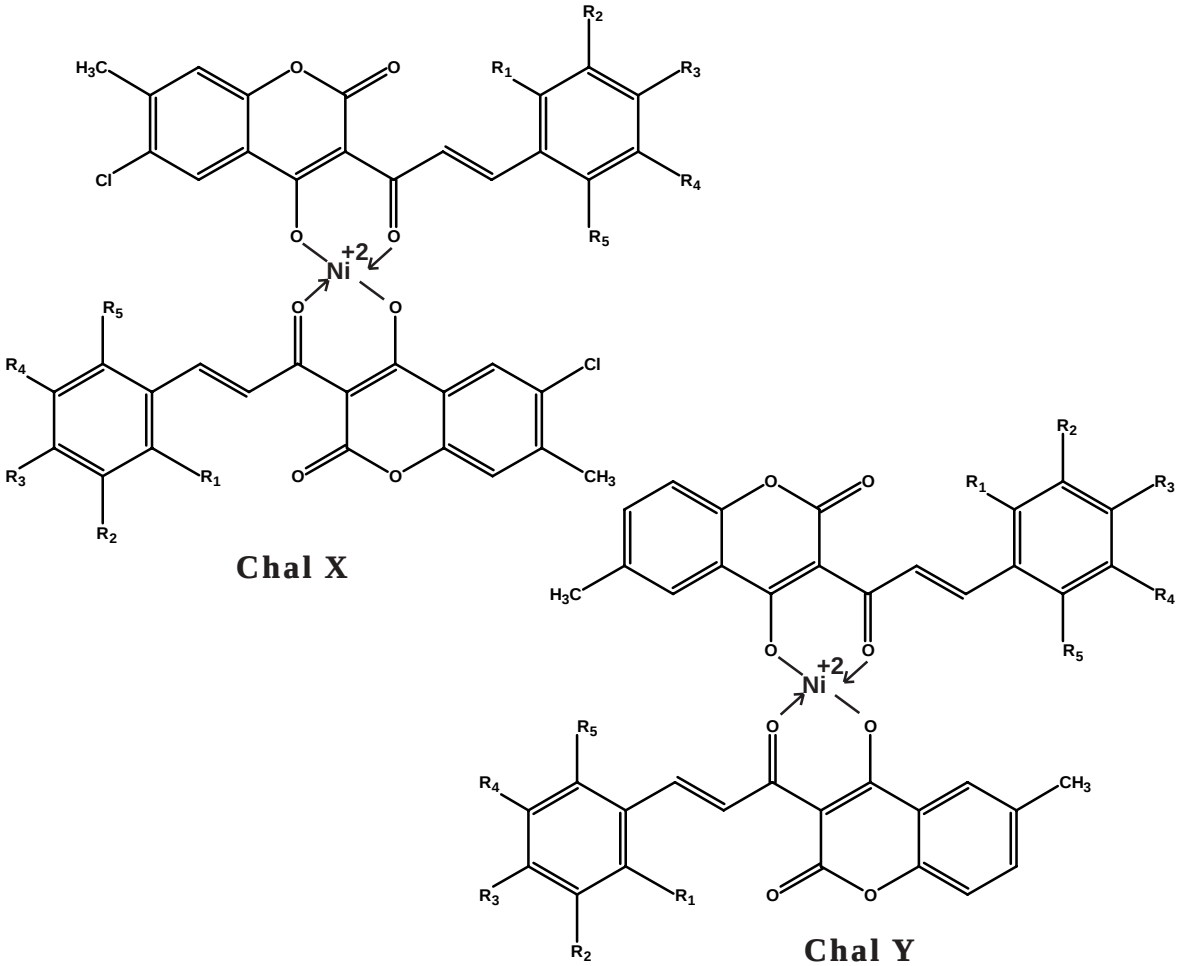
Nickel complexes:

All the nickel complexes are insoluble in water and slightly soluble in alcohol and other organic solvents. On the basis of elemental analysis these complexes are found to be of ML_2 type.

All absorption spectra of nickel complexes show two absorption band at 315-370 nm., 501-550 nm. Along with the ligand bands (shifted). The crystal field diagram for the tetragonal Ni(II) (d^8) complexe is as under.



It is fully filled up to a_1g orbital. The ground term is A_1g. Excitation of one of the a_1g electron to the b_1g orbital leads to ^3B_1g and ^1B_1g terms, but the transition form $^1A_1g \rightarrow {}^1B_1g$ is spin forbidden and hence band at 501-550 nm. is attribute to the transition $^1A_1g \rightarrow {}^1B_1g$. The other band at 315-370 nm. is attribute to $^1A_1g \rightarrow {}^1B_1g$. The excitation coefficients of these two bands are large in spite of the Laporte - forbidden. It is because of the extensive mixing of metal 'd' orbitals and the ligand orbitals. The magnetic susceptibility measurements show that all nickel complexes are diamagnetic. The low value of conductivity shows that the complexes are non ionic in nature.



Chal X

Chal Y

Where R_1, R_2, R_3, R_4 & R_5 are described on page 209.

Cobalt complexes:

All the cobalt complexes are in soluble in water and slightly soluble in alcohol and other organic solvents. On the basis of elemental analysis these complexes are found to be of ML_2 type.

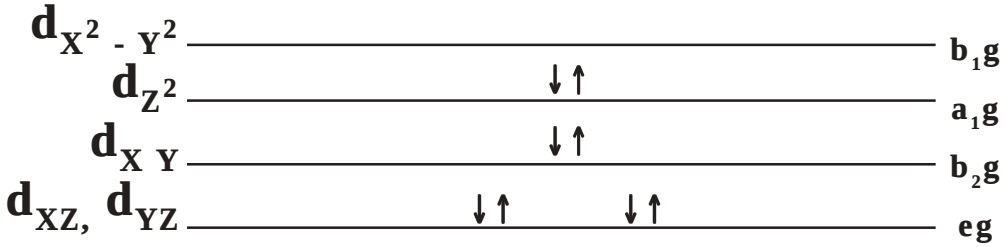
The magnetic susceptibility of the complexes was measured at room temperature by GUOY balance method and corrected for diamagnetisms using Pascal's constants. They are found to be paramagnetic and have μ_{eff} values between 1.89 - 2.03 B.M.

The molecular weight determination by the Rase Camphor method although not very reliable still it is in agreement with suggested molecular formula of the complexes.

The conductivity of the solution of the cobalt complexes in DMF was measured and low value of conductivity observed, suggest that the metal complexes are non ionic in nature.

Absorption spectra:

The absorption spectra of these compounds show only one band at 848-898 nm. along with the ligand bands. The crystal field diagram for Co(II) d^7 in D_4h symmetry is as below.

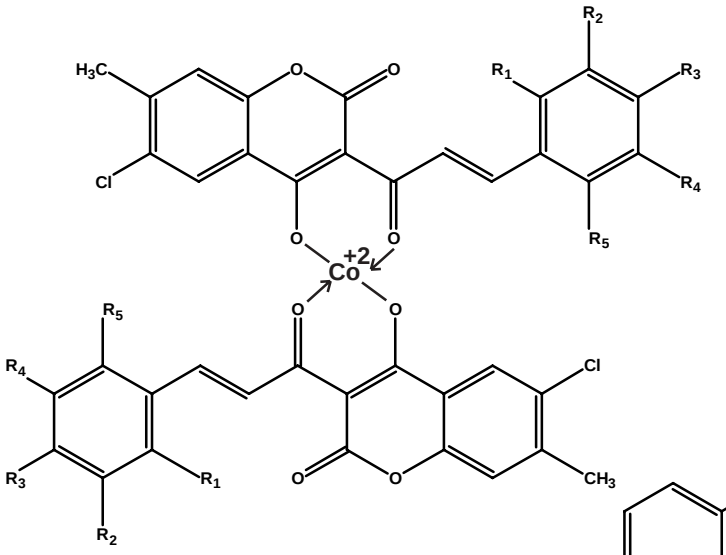


There is one unpaired electrons in a_1g orbital. The ground term is $2A_1g$. The transition corresponding to $^2A_1g \rightarrow {}^2B_1g$ and $^2A_1g \rightarrow {}^2Eg$ are expected. In this case only one absorption maxima is observed at 848 - 898 nm. Which can be attribute to $^2A_1g \rightarrow {}^2E_1g$ transition. However the absorption maxima is not clear in the figure. The reason may be the broad bending of the band so that exact location of the λ max could not be seen.

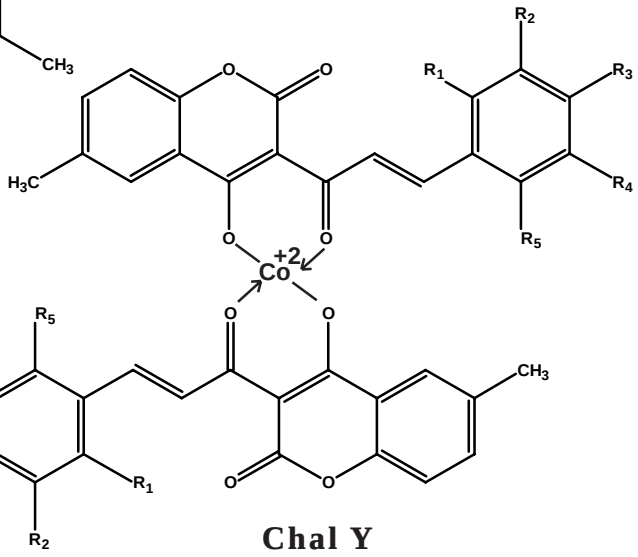
Magnetic property:

The cobalt complexes are paramagnetic having the unpaired electron. Generally the magnetic moment for square planner Co(II) is of the order of 1.89 to 2.03 B.M. which is attribute to maxima of the higher ligand field terms in to the ground $2A_1g$ term by spin orbital coupling to give some orbital contribution to the moment. However remarkably high moments of the Co(II) square planner complexes could not be explained satisfactorily.

Generally Co^{+3} state is more stable and there is tendency of Co(II) to convert in Co(III) but here Co(II) might have stabilized due to the conjugation of the ligand. The possible structure of the Cobalt complexes are as under....



Chal X



Chal Y

Where R_1, R_2, R_3, R_4 & R_5 are described on page 209.

Iron complexes:

All the iron complexes are stable at room temperature. They are soluble in water and slightly soluble in alcohol and other oragnic solvents.

From the elemental analysis and TGA, it is found that iron complexes are of the $ML_2(H_2O)_2$ type. The molecular weight determination by Rast Camphor method although not very reliable still it is in agreement with the suggested molecular formula of the complexes.

The conductivity of the solution of iron complexes in DMF was measured and low value of conductivity observed suggest that the metal complexes are non ionic in nature.

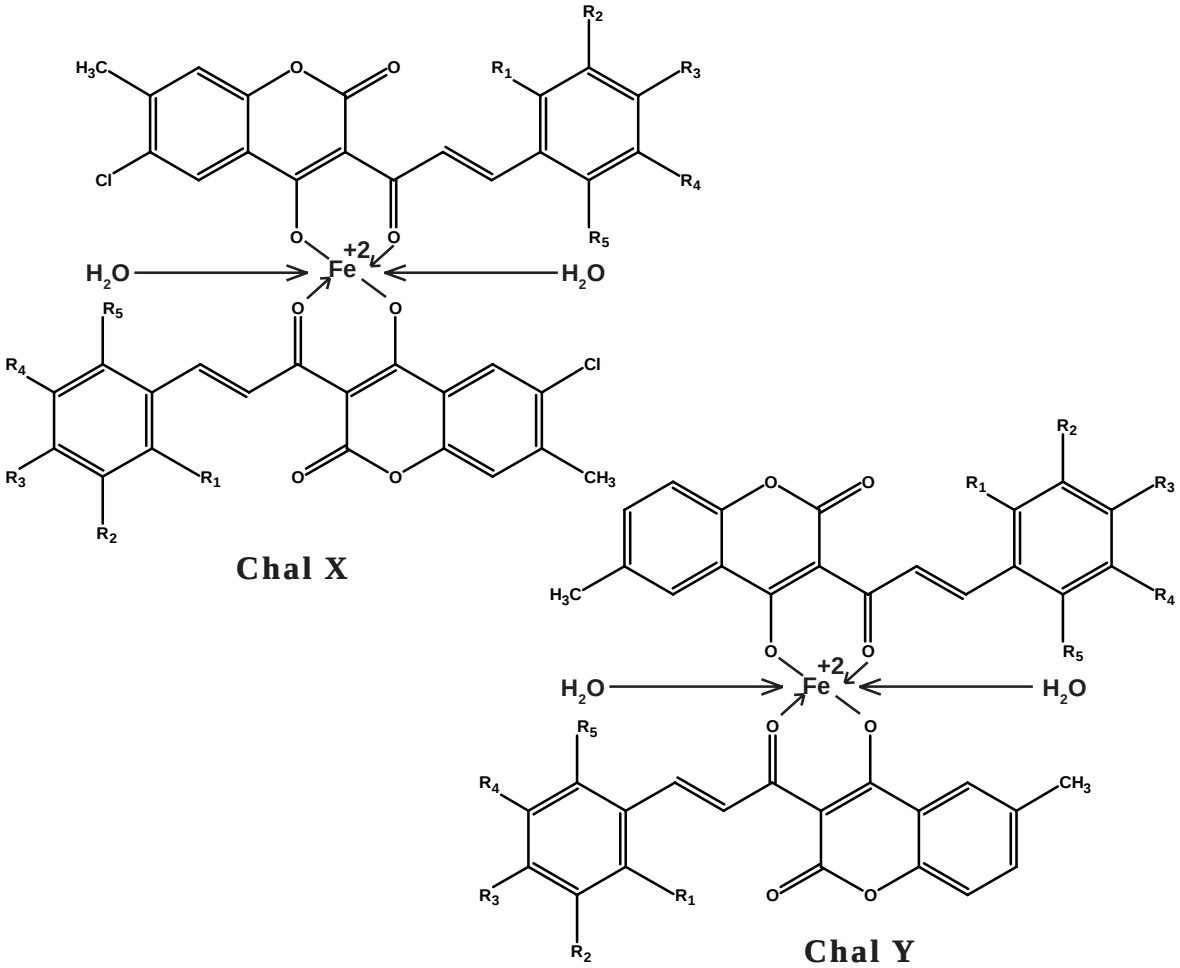
Absorption spectra and magnetic properties:

These complexes are diamagnetic. The ground state ^1A_1g. Their absorption spectra show only one band at 938-969 nm. It is a weak band, which is probably due to the transition. $^2A_1g \rightarrow {}^2T_1g$. The spectra are not much clear and more broadening is the cause for depending the fine structure of the spectra.

The Fe(II) complexes are suppose to have destorted octahedral arrangement where two water molecules coordinated with Fe(II) ion are present in trans position.

Generally Fe^{+3} is very stable as compared to Fe^{+2} state, therefore Fe^{+2} has a tendency to oxidize into Fe^{+3} state. In our case to as certain whether Fe^{+2} has converted to Fe^{+3} during the preparation of the complex. We took the help of magnetic susceptibility of the complexes.

It is found that the complexes are diamagnetic in nature, which support Fe^{+2} state in the complex because had it been in Fe^{+3} state the complex should be paramagnetic. The possible structure of iron complex are as under.



Chal X

Chal Y

Where R_1, R_2, R_3, R_4 & R_5 are described on page 209.

Stability constants of Metal complexes :

The practical proton ligand and metal ligand stability constants were determined by Calvin-Bjerrum titration technique[2] using nitric acid and constant ionic strength was maintained with sodium nitrate. The method is valid both in water dioxane medium. The titration ion has very slight complexing tendency and the comparison between nitrate ion and the ligand under study of minor importance.

The pH meter was calibrate with aqueous buffer and to keep metal complex in homogeneous medium, the water **:** dioxane **::** 40 **:** 60 was used as solvent and the true value of pH corresponding to aqueous solution was calculated from the pH meter reading by using Van-Uitret and Hass[5] relation method.

Proton-ligand stability constant :

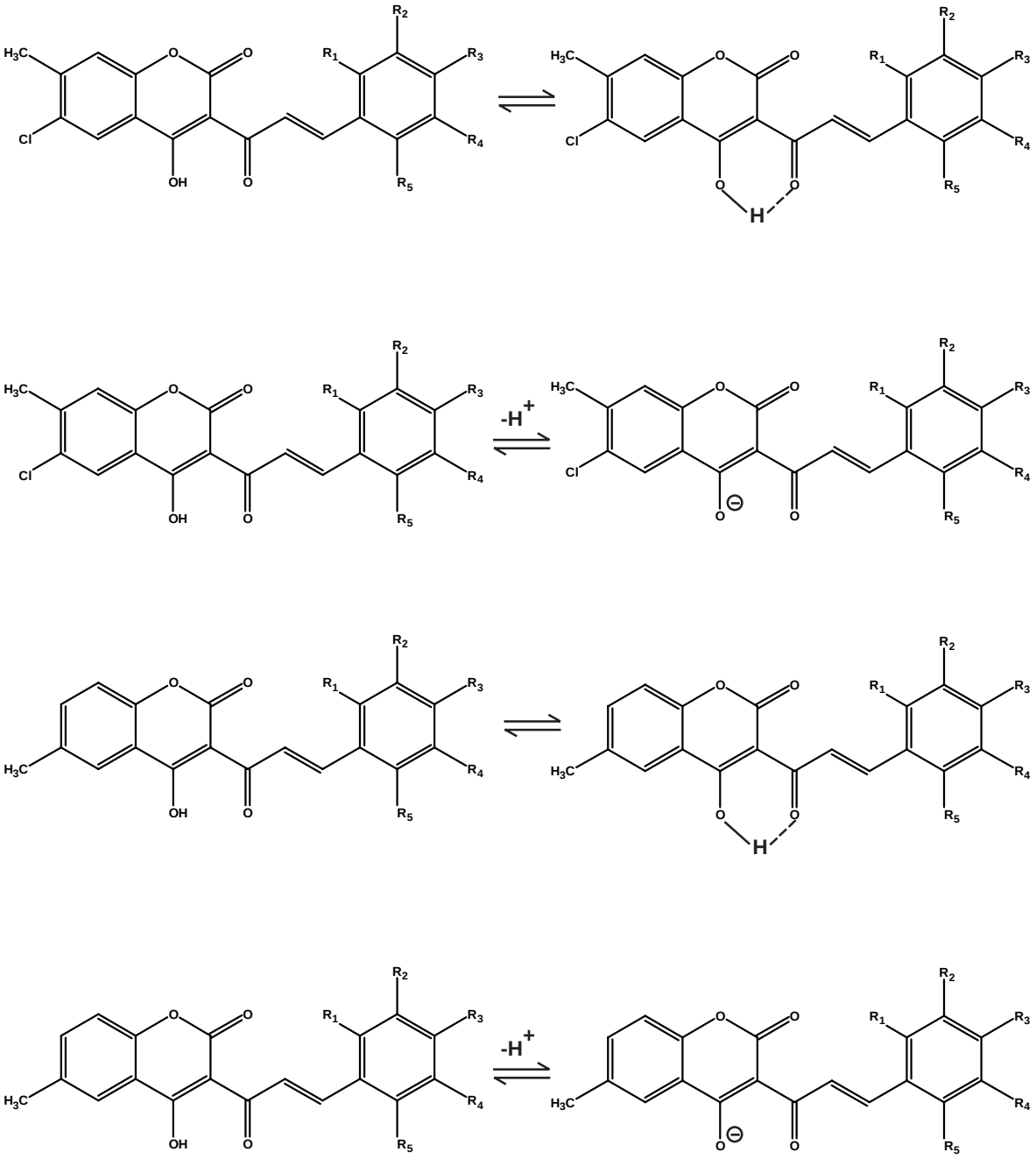
The ligands have one phenolic group. They are associated with intramolecular hydrogen bond between carbonyl group (C=O) and phenolic oxygen. The proton-ligand stability constant influenced by various factors like general polar effects, effect of mass, steric influence and effect of substituents.

All the value of proton-ligand stability constants considered in this discussion part were obtained by laest square method at $30^{o} \pm 0.2^{o}C$.

The association of proton is affected by strength of hydrogen bonding between oxygen of hydroxyl group and carbonyl group (C=O) of the acetyl or acetoacetyl. Stronger the hydrogen bond, lesser will be the dissociation and hence less is the acidic character of -OH group.

Ligand-titration curves:

It was observed that in the initial stage of the titration the ligand curves shifted to the lift (or above) the acid titration curve. The protonated species so formed dissociated in two steps as shown on next page.



Where R_1, R_2, R_3, R_4 & R_5 are described on Page No. 209.

The addition of alkali was accompanied by a gradual change in colours of the solution from pale yellow to dark yellow orange. The pale yellow colour might be due to the formation of protonated species, where as the drak yellow orange colour due to anion. The log pK_1^H and log pK_2^H correspond to the species LH and LH_2 respectively.

Metal titration curves:

In all the systems under investigaton the metal titration curves were depressed below the ligand titration curves.

This was expected in the complex formation of the metal ion with the ligand. During the metal titration in presence of excess of the ligand (nearly five times more).

The metal hydroxide was not precipitated even at a pH value higher than that of hydrolysis of the metal ion. The metal ion hydrolysis if present can lead to too high value of stability constants. The pH of metal hydrolysis in 60-40% dioxane-water the reagent curves in the different system investigaged at $30^o \pm 2^oC$ are summarized below.

Metal	B of hydrolysis	B of departed metal curve.			
		1	2	3	4
Cu (II)	5.35	4.70	4.85	4.60	4.68
Ni (II)	5.90	5.60	5.68	5.53	5.75
Co (II)	6.60	6.15	6.40	6.28	6.55
Fe (II)	7.15	6.75	6.88	6.63	6.71

In view of very low ($0.1x10^{-3}$ M) concentration of the metal ion used in titration, formation of polymolecular complexes may be considered unimportant, although, the titration data, on their own cannot yield any information about the presence of such species.

The possibility of information of hydrogen bearing complexes which might arise, can be neglected on the ground that the potential proton bearer phenolic oxygen and carbonyl group of acetyl will be involved in bond formation with the metal ion and so they cannot be expected to hold proton.

In order to minimize the interference due to anion complexing, the general practice is to employ either perchlorate or nitrate as source for ion. It is believed that nitrate ion has a very small tendency to form complexes with metal ion especially organic solvent to the same extent for all systems and therefore not likely to invalidate the comparison of the log K value.

Stability constants of metal complexes and its variations with the nature of ligands :

The metal ligand formation curve (fig. A-3, B-3, D-3, E-3 & on page165, 176, 187, 198) for copper complexes in all systems studies show that the $\bar{n}$ values lie beween 0.096 to 1,93 indicating the formation of 1:2 complex of the type ML_2. The stability constants of the copper complexes were determined by various computational methods as described earlier on page 147 to 150. There is a relatively large difference betwen log β_2 of Cu(II) and those for the complexes of other metal ions in each system. Thus, it was observed that copper complexes were stable than other corresponding metal complexes. Similar observations have made by other worker[28]. The higher relative stability of copper chelates might be attributed to the planer configuration commonly observed for Cu(II) complexes.

Similarly, the formation curves for Ni(II), Co(II) and Fe(II) show 1:2 complexation and their stepwise stability constants were determined by various computational methods described on page 147 to 150. The behaviour of stability constant with different ligands was similar to copper complexes.

Variation of chelate stability with the nature of metal ions:

This may be studied by comparing the stabilities of complexes of series of metal ions with a give ligand. For a given ligand, irrespective of its nature, the order of stability constants of complexes of bivalent ions of the first titration series are usually in the natural order (called the Irving - Williams order[29]).

$$Cu(II) > Ni(II) > Co(II) < Fe(II)$$

Variation of this order had been attributed to the formation of low spin complexes stereo chemical consideration and entropy factors.

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